http://dx.doi.org/10.5935/0103-5053.20130236

J. Braz. Chem. Soc., Vol. 24, No. 11, 1711-1718, 2013.
Printed in Brazil - ©2013 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Review

Analytical Methods to Assess Carbonyl Compounds in Foods and Beverages

Vanessa M. Osório and Zenilda L. Cardeal*

Departamento de Química, Universidade Federal de Minas Gerais, 31270901 Belo Horizonte-MG, Brazil

Compostos carbonílicos, tais como os aldeídos, são amplamente encontrados em produtos alimentares. Estes compostos podem originar-se de matérias-primas, fermentação alcoólica ou como produtos de uma grande variedade de reações químicas. Este *Review* apresenta estudos realizados para determinar contaminantes de aldeído em produtos alimentares. Entre os métodos utilizados para avaliar a presença de aldeídos em alimentos e bebidas, os mais citados são os métodos cromatográficos. Técnicas cromatográficas empregadas incluem a cromatografia líquida de alta eficiência com detecção ultravioleta, cromatografia gasosa com detecção por ionização em chama e com detecção de espectrometria de massas. Métodos de amostragem e o potencial de uso da microextração em fase sólida para determinação de substâncias químicas nos alimentos também são discutidos neste artigo.

Carbonyl compounds, such as aldehydes, are widely found in food products. These compounds can originate from raw materials, alcoholic fermentation or as products of a wide range of chemical reactions. This Review presents studies performed to determine aldehyde contaminants in food products. Among the methods used to evaluate the presence of aldehydes in food and beverages, chromatographic methods are the most commonly cited. Employed chromatographic techniques include high performance liquid chromatography with ultraviolet (UV) detection, gas chromatography with flame ionization detection and with mass spectrometry detection. Sampling methods and the potential use of solid phase microextraction for determining chemical substances in foods are also discussed.

Keywords: aldehydes, food contamination, derivatization, chromatography methods

1. Introduction

Many studies have raised concerns regarding indoor air pollution due to carbonyl compounds released by various sources. Such sources include cigarette smoke and the burning of oils, animal fats and vegetables.[1]

Carbonyl compounds are widely found in food products, such as fried foods and beverages (wine, vodka, beer and cognac). The formation of carbonyl compounds is caused by the oxidation of fatty acids and higher alcohols, Strecker degradation, aldol condensation, or Maillard reactions. A number of these reactions has received considerably more attention than others.[2]

The toxicity of low molecular weight carbonyl compounds, such as aldehydes, to humans and animals is well-known. Both the International Agency for Research on Cancer (IARC) and the US Environmental Protection Agency (US EPA) classified formaldehyde as "carcinogenic to humans" in group 1. The US EPA sets the acceptable daily intake (ADI) of formaldehyde to 0.2 mg kg^{-1} body weight and warned of potential adverse health effects resulting from intakes of formaldehyde at levels higher than ADI. Acetaldehyde is also toxic, an irritant and a probable carcinogen.[3]

Although it is known that aldehydes can be found in certain foods, the quantity contained and the typical amounts ingested have not been studied. Little is known about the health risks from exposure to aldehydes in fried foods, mainly due to the lack of appropriate methods to measure aldehyde presence.

This Review focuses on studies published that deal with the development or application of gas chromatography (GC) and high performance liquid chromatography (HPLC) techniques for the determination of aldehydes in different food matrices.

*e-mail: zenilda@ufmg.br

2. Sources of Exposure and Toxic Effects of Aldehydes

Aldehydes are released into the atmosphere by either natural or anthropogenic sources. The most significant anthropogenic sources are automobile exhaust and equipment in which hydrocarbon fuels are incompletely burned. Forest fires and volcanic gases are the mainly natural sources to introduce aldehydes into the environment.[4]

Industrial and manufacturing processes, power plants that burn fossil fuels, forest fires and open burning of wastes and vegetation can also introduce aldehydes into the atmosphere. People may also be exposed to aldehydes at high concentrations in the indoor environment. Such sources as combustion appliances, tobacco smoke and frying emitted aldehydes in substantial amounts. As a result, indoor aldehyde concentrations almost always exceed outdoor concentrations.[4]

The principal effect of human exposure to aldehydes at low concentrations, particularly acrolein and acetaldehyde, is irritation of the eyes, skin and mucous membranes of the upper respiratory tract. Aldehydes with high molecular weights, such as chloroacetaldehyde, valeraldehyde, furfural, butyraldehyde, glyoxal, malonaldehyde, benzaldehyde and synapaldehyde, appear to be less toxic than acetaldehyde and acrolein. Several studies examining these high molecular weight aldehydes are found in the literature.[5]

In foods, particularly beverages, the presence of aldehydes is common and may be detrimental to the quality of the product. Carbonyl compounds in foods are related to such problems as nausea, vomiting, restlessness, sweating, confusion, drops in blood pressure and headaches.[6] The presence of low molecular mass carbonyls (C_1-C_6) in spirits and alcoholic beverages is undesirable because they can be responsible for unpleasant organoleptic properties in alcoholic drinks and some health implications. These carbonyls can bind *in vivo* to biological nucleophiles, resulting in toxic mutagenic and carcinogenic effects.[6] On the other hand, depending on their concentration and on the substance itself, carbonyl compounds are also considered important flavor components.[7]

The study of volatile organic compounds (including aldehydes) formed during the heating of cooking oils shows that the oil fumes resulting from heating edible oils such as rapeseed oil, soybean oil, peanut oil and lard exhibit mutagenicity and genetic toxicity.[8] Moreover, medium and short chain aldehydes are responsible for the unpleasant odors in fat-rich foods that have gone rancid.[9]

The formation of carbonyl compounds during the storage of beer has been the subject of extensive investigation for a considerable length of time.[10] The flavors of beer, cider and wine all change during storage. The development of stale flavor notes is usually accelerated by storage at elevated temperatures. Wort, the liquid extracted from the mashing process during the brewing of beer or whisky, contains a complex mixture of carbonyl compounds that contribute to its characteristic malty flavor.[11]

During fermentation, the majority of carbonyl compounds present in wort are transformed into other molecules, e.g., alcohols, which are generally much less flavor active than the corresponding aldehydes and ketones.[12] Fresh beer usually contains low levels of carbonyl compounds (approximately 40 pg L^{-1}), and even after prolonged storage, the majority of aldehydes and ketones present are at concentrations substantially below their flavor thresholds.[12]

The formation of carbonyl compounds in beer has interested brewing chemists in recent years. Four main formation pathways for carbonyl compounds have been determined. These pathways are the Strecker degradation of amino acids, the oxidation of alcohols and the autoxidation of fatty acids.[13] The Strecker degradation of α-amino acids results in the formation of an aldehyde containing one less carbon atom than the amino acid precursor.[14] Dicarbonyl compounds are formed as intermediates during the reaction of sugars and amino compounds. These compounds subsequently react with amino acids to form aldehydes; for example, iso-valeraldehyde is formed from leucine via this reaction. However, the amounts of simple aldehydes, such as formaldehyde, acetaldehyde and iso-butyraldehyde, produced by such reactions are far too small for these compounds to contribute to beer staling.[13]

Unsaturated carbonyl compounds are known to be formed by lipid peroxidation in many foods (e.g., milk, butter and vegetable oils). These compounds are directly associated with various diseases, including cancer, mutagenesis, Alzheimer's, aging, arthritis, inflammation, diabetes, atherosclerosis and AIDS.[15]

The autoxidation of unsaturated fatty acids, such as linoleic acid and arachidonic acid, to produce aldehydes is well-known. Heat treatments, including cooking, frying and other food preparation processes, can cause the oxidation of lipids. Bastos and Pereira[16] have proposed a mechanism for the formation of acrolein by the oxidation of linoleic acid.

Figure 1 describes the mechanism for the formation of secondary products from the oxidation of lipids as reported by Shibamoto.[15]

Acrolein is one of the most acutely toxic and highly irritating aldehydes commonly present in food. Acrolein can be formed in various ways and is found in many different foods and beverages.

The cider alteration, also known as *piqûre acroléique*, results from the chemical transformation of

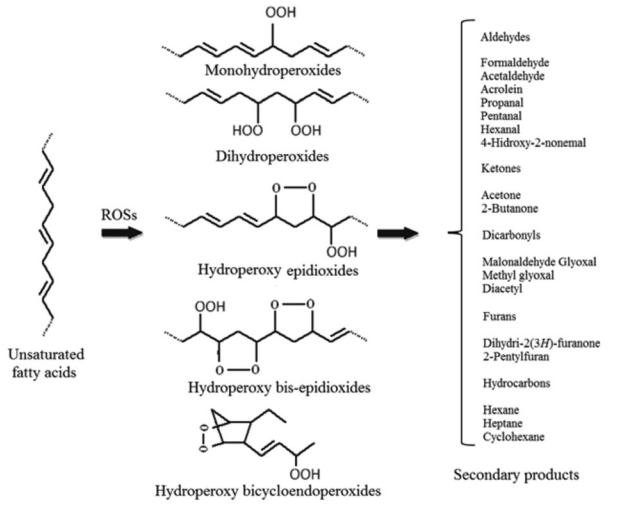

Figure 1. Mechanisms reaction for the formation of secondary products from the oxidation of lipids.

3-hydroxypropionaldehyde (3-HPA) into acrolein, a lachrymatory agent responsible for undesirable peppery flavors. The 3-HPA precursor of acrolein is derived from glycerol, one of the most important byproducts of alcoholic glucose fermentation by yeast. As shown in Figure 2, glycerol is converted into 3-HPA by a coenzyme B12-dependent dehydratase as described by Sauvageot *et al.*[17]

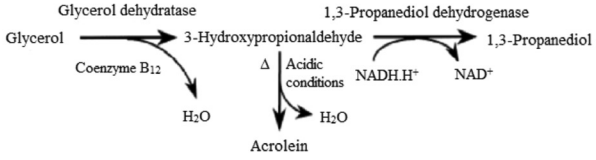

Figure 2. Metabolic pathway for the conversion of 3-hidroxipropanal to acrolein.

According to the World Health Organization (WHO), concentrations of acrolein in food are generally less than 40 mg g^{-1}, with the highest found concentrations being 1 mg g^{-1} or less.[18] The US Food and Drug Administration (US FDA)[19] determined that the levels of acrolein used to prepare modified food starch should not exceed 0.6% m m^{-1}.

The US EPA[20] states that for the protection of human health from ingestion of acrolein in water or in contaminated aquatic organisms, the concentration should be no more than 0.320 or 0.780 mg L^{-1}, respectively.

The olfactory perception threshold of acrolein in the environment is 0.21 mg L^{-1}. Concentrations ten times higher are considered dangerous to life and health.[21]

3. Derivatization Methods of Aldehydes

The use of a derivatizing agent in conjunction with a chromatographic separation method and analysis is sometimes necessary to improve the chromatographic properties and/or the sensitivity of the detection method. Many polar analytes need to be derivatized before gas chromatographic separation, either to increase their volatility and thermal stability or to decrease their adsorptivity.[22] There are a large number of derivatizing agents for the analysis of aldehydes, including 2,4-dinitrophenylhydrazine (2,4-DNPH), 2,4,6-trichloro-phenylohydrazine (TCPH), cysteamine (2-aminoethanethiol), *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA) and morpholine. The most common derivatization agent for aldehydes is 2,4-DNPH.

The specific reaction of carbonyl compounds with DNPH that results in the formation of the corresponding 2,4-dinitrophenylhydrazone is one of the most important qualitative and quantitative methods used in organic analysis. This method has been used to measure aldehydes and ketones in urine[23] and other biological samples,[24] as well as environmental air[25] and water samples.[26] The reaction of 2,4-DNPH with carbonyl compounds is presented in Figure 3.

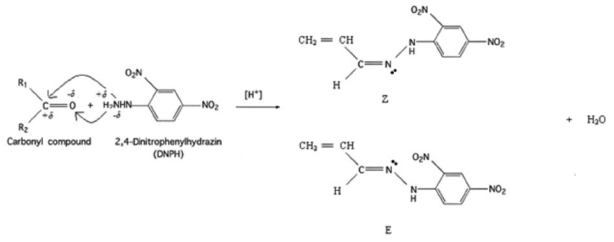

Figure 3. Reaction of 2,4-DNPH with carbonyl compounds to form hydrazones.

The main advantage of 2,4-DNPH derivatization is the ability to analyze a complex mixture of various aldehydes and ketones simultaneously.

When selecting a derivatizing agent for carbonyl compounds, it is important to take into account the following criteria:

(*i*) A stable product must be formed in the reaction between the reagent and the analyte.

(*ii*) The velocity of the reaction between the reagent and the analyte must be sufficiently high to achieve a quantitative reaction.

(*iii*) A high degree of volatility of the derivatives is favorable for gas chromatographic analysis, and vaporization without decomposition is essential.

4. Derivatization by SPME

More recent work has utilized SPME, the main focus of this article. Other extraction techniques may also be used for analysis of carbonyl compounds in foods.

Stashenko *et al.*[9] compared liquid-liquid extraction (LLE) with solid phase extraction (SPE) for the analysis of carbonyl compounds in various heated vegetable oils (corn, palm or sunflower). The authors concluded that higher reproducibility and recoveries of volatile aldehydes were obtained by using SPE.

Since solid phase microextraction (SPME) was introduced by Arthur and Pawliszyn,[27] it has been widely applied to environmental, food and biological analysis in combination with GC, HPLC and capillary zone electrophoresis (CE).

SPME is an extraction technique commonly used during the analysis of aldehydes by gas chromatography. The SPME technique is based on the establishment of equilibrium between the analyte and a fused silica fiber coated with a stationary phase. This stationary phase can be a liquid polymer, a solid sorbent or a combination of both. The analyte is subsequently desorbed from the fiber into the injector of a chromatography system. This technique is extremely attractive because it combines analyte sampling and pre-concentration into a single step and allows direct desorption to the chromatographic system. Other SPME benefits include low analysis cost, simplicity of operation, fiber reuse, portability, ease of operation and automation, minimal sample loss and lack of contamination during transport and storage and a wide variety of phases that are applicable to many different compounds.

Using SPME, derivatization can occur in the sample matrix, on the SPME fiber after sampling or simultaneously. Derivatization in the sample matrix can occur either in headspace mode, in which the fiber is exposed to the vapor phase above a solution, or by direct immersion in the solution. Derivatization on the SPME fiber after sampling begins with exposure of the fiber to analyte solution. After this step, the fiber, loaded with analyte, is exposed to the derivatizing reagent solution or headspace, and derivatives are formed on the fiber. In on-fiber derivatization, the fiber is saturated with the derivatization agent and subsequently immersed into the solution or headspace mode of sample, in which analytes are absorbed and derivatized simultaneously.[22]

Saison *et al.*[28] used SPME and gas chromatography coupled with mass spectrometry (GC/MS) to determine the amounts of carbonyl compounds in beer by derivatization with PFBHA utilizing a PDMS/DVB fiber. The authors compared the extraction efficiency of on-fiber and in-solution derivatization. The results demonstrated that in-solution derivatization gave better extraction efficiencies.

Headspace solid-phase microextraction was used in both with and without on fiber derivatization to determine the amounts of carbonyl compounds in fish species. PFBHA was used as a derivatizing reagent to form oximes. Carbonyl compounds were analyzed by GC/MS. A comparison showed that the on-fiber derivatization method was more efficient for the detection of all of the target carbonyls in ripened anchovy.[29]

Osório and Cardeal[30] developed an SPME sampling method by immersion after derivatization in solution with 2,4-DNPH to determine the amounts of acrolein formed during frying in soybean, corn, canola, sunflower and palm oils. The hydrazones formed were analyzed by GC/MS. The results showed that changes in acrolein concentration occurred after frying potatoes in different types of oil and with different frying cycles. Potatoes fried in soybean oil contained the lowest concentration of acrolein.

5. Analytical Methods for the Determination of Aldehydes

For the analysis of aldehydes, several methods have been used, and almost all are based on the reactivity of the carbonyl group through derivatization steps and/or colorized products. Extraction methods developed for volatiles aldehydes are normally dependent on the analysis method chosen after the extraction step. Because of the reactivity of aldehydes, a derivatization step can be used to protect the chemical structure.

Due to their potential adverse health effects, there is still a great demand for reliable, sensitive and specific methodology for the determination of aldehydes in different foods.[7] HPLC and GC methods for the determination of aldehydes are the most convenient techniques.[31]

GC/MS is a useful methodology. Despite the poor chromatographic and mass spectrum properties of higher aldehydes, most analytical methods for their determination are based on gas chromatography with electron-capture detection (GC/ECD) of chemical derivatives. Various GC detectors can be used for the determination of carbonyl compounds. High resolution gas chromatography (HRGC) with ECD detection, nitrogen-phosphorus detection (NPD), flame ionization detection (FID) and mass spectrometry-selected ion monitoring (MS/SIM) were used for the analysis of eighteen different carbonyl compounds. The ECD detector had highest sensitivity with limits of detection of 16.20 and 16.90 fmol mL^{-1}, while the MS/SIM detector was the most selective.[9]

The amounts of carbonyl compounds in vodka were determined by GC/ECD using PFBHA as a derivatizing agent and SPME as an extraction technique. The developed method had a correlation coefficient of 0.9799 (concentrations ranging from 0.32 to 8.00 mg L^{-1}) with an relative standard deviation (RSD) of 5.5%.[7]

Bao *et al.*[26] developed a method for the determination of carbonyl compounds in water. The derivatizing agent was PFBHA followed by SPME and analysis by GC/ECD. The precision of the SPME technique was determined using bidistilled water, ozonated drinking water and rainwater. The limits of detection (LOD) were similar (0.006-0.200 μg L^{-1}) using GC/ECD for carbonyl compounds with SPME immersed in the liquid or in headspace mode. The author compared SPME with LLE and concluded that for all carbonyl compounds studied, both SPME modes were in good agreement with the values obtained by LLE.

Also utilizing PFBHA as a derivatizing agent, Ochiai *et al.*[32] determined the amounts of stale-flavor carbonyl compounds in beer by stir bar sorptive extraction (SBSE) with *in situ* derivatization followed by thermal desorption GC/MS. The method showed good linearity over a concentration range of 0.10 to 10.0 g L^{-1} for all analytes. The limits of detection ranged from 0.021 to 0.032 g L^{-1}.

In another study, carbonyl compounds were analyzed in spirits. Expensive vodkas were compared to cheaper vodkas using a headspace and GC/ECD method with PFBHA as a derivatizing agent and derivatization in solution to form oximes. The analysis confirmed that the more expensive vodkas contained considerably smaller amounts of carbonyl compounds, primarily less acetaldehyde, crotonaldehyde and acrolein.[33]

In LC methods, DNPH derivatizations are performed under acidic conditions, and the 2,4-DNP hydrazone derivatives are quantitated using UV detection near 360 nm (depending on the absorption maximum wavelength of the specific hydrazone). Azevedo *et al.*[34] developed a LC method with UV/Vis detection (λ at 365 nm) and 2,4-DNP derivatization to the quantification of C_1-C_8 aldehydes in white wine (Moscato Canelli) and red wine (Shiraz) produced in the São Francisco Valley, in the northeastern region of Brazil. The proposed method presented good validation parameters to the routine analyses of aldehydes in wine.

DNPH was the derivatizing agent used to determine the amounts of aldehydes released from frying foods. The hydrazones produced by the derivatization process were separated and quantified using C18 reversed-phase liquid chromatography. The identities of the compounds analyzed were confirmed by GC/MS. Samples were collected during the preparation of fried codfish and doughnuts at temperatures of 182 and 204 °C. The results showed that there were no differences in aldehyde content from fish fillets fried at 182 or 204 °C. Cake doughnuts contained higher acrolein contents than yeast-raised doughnuts prepared under similar conditions.[35]

Fujisaki *et al.*[36] analyzed aldehydes in the exhaust of frying oil by heating the oil (180 ºC) under four levels of oxygen atmosphere (2, 4, 10 and 20%). The analysis was performed by HPLC after conversion to 2,4-DNPH. Aldehydes were identified by the comparison of retention times and UV spectra with authentic compounds. The total amount of aldehydes was lowest in the oil heated in an atmosphere with 2% oxygen. Acrolein was not founded in oils heated in the atmosphere with 2% oxygen.

In another study of aldehydes released from fried foods, Osório and Cardeal[30] developed a GC/MS method, also using 2,4-DNPH as a derivatizing agent, to quantify acrolein in French fries prepared in varying types of frying oils. The method was validated and found to be precise (RSD of 9.6%), sensitive (LOD of 0.84 ng g^{-1} and limit of quantification (LOQ) of 1.40 ng g^{-1}) and linear in the range of interest (1.0-18.0 mg L^{-1}, $r^2 = 0.994$). The results showed that the concentration of acrolein in French fries depends on the viscosity of the oil, the fatty acid content and absorption of the oil by the food.

The analyses of carbonyl compounds in meat are accomplished through derivatization reactions with carbonyl protein. Resconi *et al.*[37] analyzed carbonyl compounds in meat from lambs using PFBHA derivatization with GC/MS and gas chromatography-olfactometry (GC-O) analyses. In this study, it was used a dynamic headspace-solid phase extraction (DHS-SPE) to sampling the volatile compounds of lamb before performing the derivatization in cartridges (Lichrolut EN[â] resins). The most important aroma compounds determinate were Strecker aldehydes and ketones.

DNPH was used to determine the amounts of aldehydes in smoked salmon, frankfurter, steak, and pork chop. This study[38] presents an on line SPE UHPLC-MS/MS method for the simultaneous determination of PAHs and aldehydes. The authors show that even using a multi-step method of sample preparation, the matrix effect is expressive.

Meat analyses also include the determination of unsaturated aldehydes that are produced from protein carbonyl oxidation. The determination of α-aminoadipic (AAS) and γ-glutamic semialdehydes (GGS) in a meat system is based on LC methods. Armenteros *et al.*[39] analyzed AAS and GGS by liquid chromatography--electrospray ionization-mass spectrometry (LC-ESI-MS) using DNPH derivatization method to prove that the carbonyl protein oxidation is dependent on the lipid composition and structure of the meat product. Utrera *et al.*[40] used a derivatization procedure with *p*-amino-benzoic acid (ABA) followed by fluorescent HPLC to analyze AAS and GGS in burger patties showing the oxidation pathways of meat carbonyl.

Table 1. Analysis methods and derivatizing agents used to determine aldehyde concentrations in food

Derivatizing agent	Type of derivatization	Matrix	Analytical technique	Reference
PFBHA	on fiber	beer	GC/MS	32
		fish	GC/MS	29
		sunflower oil	GC/MS	22
PFBHA	solution	grape pomace distillate	GC/MS	51
Morpholine	solution	beef fat	GC-NPD	52
N-Methylhygrazine	solution	vegetable oil	GC-NPD	53
DNPH	solution	fresh fry	GC/MS	30

Table 1 presents other publications that address the determination of aldehydes in foods utilizing various derivatizing agents.

Analysis of aldehydes in food is of great concern because they can be harmful even at low concentrations. Therefore, methods of comprehensive two-dimensional chromatography, which enable quantitation at trace levels, are a viable alternative of food analyses.[41,42]

GC×GC is thus a consolidated technique to analyze complex matrices. Nevertheless, its application in analyzing aldehydes is still poorly reported. Studies employing this technique in the analysis of aldehydes in foods are mostly qualitative. Spanik *et al.*[43] used SPME GC×GC/TOFMS (time-of-flight mass spectrometry) to characterize volatile organic compounds in honeys of different botanical origins. It was possible to detect aldehydes in all honeys studied. Also using SPME with GC×GC/TOFMS, other studies report the characterization of volatile components in beverages such as wine,[44-46] cachaça[47,48] and liquors [49,50] showing the presence of aldehydes in the analyzed samples. In the GC×GC applications of aldehydes described in the literature, the samples were not derivatized.

6. Conclusions

Aldehydes are compounds of special interest among emitted volatile compounds because of their toxicity and carcinogenicity. Aldehydes can be present as contaminants in many foods, such as oil, beer, vodka and water.

Despite the common presence of aldehydes in food, there are few published studies examining them. It is especially important to establish reliable methods for the determination of aldehyde concentrations in foods. Aldehydes can be measured using different derivatization strategies and various chromatographic methods, including GC/MS, GC-ECD, GC-FID, GC-NPD or HPLC/UV. Many of the GC methods studied have used SPME with derivatization on fiber or in the solution matrix.

The different proposed methods described in the literature are effective for the determination of aldehyde concentrations in foods. Nevertheless, more studies must be performed to determine the presence of aldehydes in food, especially during frying processes or beverage production. Moreover, it is essential that the methods of analysis possess a high sensitivity for monitoring trace levels. The tendency is to use two-dimensional comprehensive GC or LC methods able to reduce matrix effects.

Acknowledgement

This study has been supported by FAPEMIG (Fundação de Amparo a Pesquisa do Estado de Minas Gerais) and CNPq (Conselho Nacional de Pesquisa e Desenvolvimento).

Vanessa M. Osorio *is an Associate Professor of the Department of Chemistry and Physics of the Federal University of Santo Esprítio (Brazil). She completed her Doctorate at the Federal University of Minas Gerais (Brazil) in 2012 with research development of methods for analysis of acrolein using gas chromatography. She researches in several areas of cromatography. Her current work is focused in the determination of volatile compounds in liquor and analysis of aldehydes in foods.*

Zenilda L. Cardeal *is an Associated Professor of the Chemistry Department of the Federal University of Minas Gerais (UFMG, Brazil). She has a MSc degree in Analytical Chemistry at the Universidade Estadual de Campinas (Brazil, 1988), PhD in Chemistry from the Université de Paris XI (Paris-Sud, France, 1993) and Post-Doctoral in the Royal*

Melbourne Institute of Technology (Australia, 2005). The main aims of her research are: development and validation of methods for environmental analyses, evaluation of the quality of environmental compartments (inside and outside) with regard to the presence of xenobiotic toxic substances, determination of toxic volatiles in food and assessment of human exposure to toxic agents. Chromatographic methods are developed and/or validated and improved for the analysis of toxic organic substances present at trace level in major environmental compartments and food. These methods are applied to monitoring and assessment of environmental and occupational exposure.

References

1. Gilbert, N. L.; Guay, M.; Miller, J. D.; Judek, S.; Chan, C. C.; Dales, R. E.; *Environ. Res.* **2005**, *99*, 11.
2. Saison, D.; De Schutter, D. P.; Delvaux, F.; Delvaux, F. R.; *J. Chromatogr., A* **2008**, *1190*, 342.
3. Kim, H. J.; Shin, H.-S.; *Anal. Chim. Acta* **2011**, *702*, 225.
4. Committee on Aldehyde; *Formaldehyde and Other Aldehydes*; N. R. C. National Academy Press: Washington, DC, USA, 1981.
5. Silva, T. O.; Pereira, P. A. D.; *J. Agric. Food Chem.* **2008**, *56*, 3129.
6. Wardencki, W.; Sowinski, P.; Curylo, J.; *J. Chromatogr., A* **2003**, *984*, 89.
7. Wang, Y.; Hossain, D.; Perry, P. L.; Adams, B.; Lin, J. M.; *Flavor Fragrance J.* **2012**, *27*, 141.
8. Katragadda, H. R.; Fullana, A.; Sidhu, S.; Carbonell-Barrachina, A. A.; *Food Chem*. **2010**, *120*, 59.
9. Stashenko, E. E.; Ferreira, M. C.; Sequeda, L. G.; Martinez, J. R.; Wong, J. W.; *J. Chromatogr., A* **1997**, *779*, 360.
10. Drost, M. K.; White, M. D.; *J. Heat Transfer.* **1991**, *113*, 823.
11. Laws, D. R. J.; Peppard, T. L.; *Food Chem.* **1982**, *9*, 131.
12. Peppard, T. L.; Halsey, S. A.; *J. Inst. Brew.* **1981**, *87*, 386.
13. Hashimoto, N.; *Brewing Science*, vol. 2; Academic Press: Waltham, Massachusetts, USA, 1981.
14. Rizzi, G. P; *Food Rev. Int.* **2008**, *24*, 416.
15. Shibamoto, T.; *J. Pharm. Biomed.* **2006**, *41*, 12.
16. Bastos, L.C.S.; Pereira, P. A. D.; *J. Agric. Food Chem.* **2010**, *58*, 12777.
17. Sauvageot, N.; Gouffi, K.; Laplace, J. M.; Auffray, Y.; *Int. J. Food Microbiol.* **2000**, *55*, 167.
18. World Health Organization (WHO), 2002, available at http://www.bvsde.paho.org/bvsacg/i/fulltext/guianca/guianca.pdf, accessed in September 2013.
19. Sajilata, M.G.; Singhal, R. S.; *Carbohydr. Polym.* **2005**, *59*, 131.
20. United States Environmental Protection Agency (US EPA); Center for Environmental Research Information: Cincinnati, OH, USA, 1999.
21. Companhia de Tecnologia e Saneamento Ambiental de São Paulo (CETESB); *Manual de Produtos Químicos Perigosos*; CETESB: São Paulo, Brasil, 2002.
22. Stashenko, E. E.; Martinez, J. R.; *TrAc: Trend Anal. Chem.* **2004**, *23*, 553.
23. Sakura, N.; Nishimura, S.; Fujita, N.; Namera, A.; Yashiki, M.; Kojima, T.; *J. Chromatogr., B: Anal. Technol. Biomed. Life Sci.* **1998**, *719*, 209.
24. Luo, X. P.; Yazdanpanah, M.; Bhooi, N.; Lehotay, D. C.; *Anal. Biochem.* **1995**, *228*, 294.
25. Dong, J. Z.; Moldoveanu, S. C.; *J. Chromatogr., A* **2004**, *1027*, 25.
26. Bao, M. L.; Pantani, F.; Griffini, O.; Burrini, D.; Santianni, D.; Barbieri, K.; *J. Chromatogr., A* **1998**, *809*, 75.
27. Arthur, C. L.; Pawliszyn, J.; *Anal. Chem.* **1990**, *62*, 2145.
28. Saison, D.; De Schutter, D. P.; Delvaux, F.; Delvaux, F. R.; *J. Chromatogr., A* **2009**, *1216*, 5061.
29. Iglesias, J.; Gallardo, J. M.; Medina, I.; *Food Chem.* **2010**, *123*, 771.
30. Osório, V. M.; Cardeal, Z. L.; *J. Chromatogr., A* **2011**, *1218*, 3332.
31. Lau, M. N.; Ebeler, J. D.; Ebeler, S. E.; *Am. J. Enol. Vitic.* **1999**, *50*, 324.
32. Ochiai, N.; Sasamoto, K.; Daishima, S.; Heiden, S.; Heiden, A. C.; Hoffmann, A.; *J. Chromatogr., A* **2003**, *986*, 101.
33. Sowinski, P.; Wardencki, W.; Partyka, M.; *Anal. Chim. Acta* **2005**, *539*, 17.
34. Azevedo, L. C.; Reis M. M.; Pereira, G. E.; Rocha, G. O.; Silva, L. A.; Andrade, J. B.; *J. Sep. Sci.* **2009**, *32*, 3432.
35. Lane, R. H.; Smathers, J. L.; *J. Assoc. Ana. Chem.* **1991**, *74*, 957.
36. Fujisaki, M.;Endo, Y.; Fujimoto, K.; *J. Am. Oil Chem. Soc.* **2002**, *79*, 909.
37. Resconi, V. C.; Mar Campo, M.; Montossi, F.; Ferreira, V.; Sañudo, C.; Escudero, A.; *Meat Sci.* **2010**, *85*, 700.
38. Gosettia, F.; Chiuminattob, U.; Mazzuccoa, E.; Robottia, E.; Calabresea, G.; Gennaroa, M. C.; Marengo, E.; *J. Chromatogr., A* **2011**, *1218*, 6308.
39. Armenteros, M.; Heinonen , M.; Ollilainen, V.; Toldrá , F.; Estévez, M.; *Meat Sci.* **2009**, *83*, 104.
40. Utrera, M.; Morcuende, D.; Rodríguez-Carpena, J. G.; Estévez, M.; *Meat Sci.* **2011**, *89*, 500.
41. Herrero, M.; Ibanez, E.; Cifuentes, A.; Bernal, J.; *J. Chromatogr., A* **2009**, *1216*, 7110.
42. Dugo, P.; Kumm, T. ; Cacciola, F. ; Dugo, G. ; Mondello, L.; *J. Liq. Chromatogr. Related Technol.* **2008**, *31*, 1758.
43. Špánik, I.; Janáčová, A.; Šusterová, Z.; Jakubík, T.; Jánošková, N.; Novák, P.; Chlebo, R.; *Chem. Pap.* **2013**, *67*, 127.
44. Welke, J. E.; Manfroi, V.; Zanus, M.; Lazarotto, M.; Zini, C. A.; *J. Chromatogr., A* **2012**, *1226*, 124.

45. Weldegergis, B. T.; de Villiers, A.; McNeish, C.; Seethapathy, S.; Mostafa, A.; Gorecki, T.; Crouch, A. M.; *Food Chem.* **2011**, *129*, 188.
46. Weldegergis, B. T.; Crouch, A. M.; Gorecki, T.; de Villiers, A.; *Anal. Chim. Acta* **2011**, *701*, 98.
47. Souza, P.P.; Cardeal, Z. L.; Augusti, R.; Morrison, P.; Marriott, P. J.; *J. Chromatogr., A* **2009**, *1216*, 2881.
48. Cardeal, Z. L.; Souza, P. P.; Siva, M. D. R.; Marriott, P. J.; *Talanta* **2008**, *74*, 793.
49. Cardeal, Z. L.; Marriott, P. J.; *Food Chem.* **2009**, *112*, 747.
50. Zhu, S.; Lu, X.; Ji, K.; Guo, K.; Li, Y.; Wu, C.; Xu, G.; *Anal. Chim. Acta* **2007**, *597*, 340.
51. Lopez-Vazquez, C.; Orriols, I.; Perello, M. C.; de Revel, G.; *Food Chem.* **2012**, *130*, 1127.
52. Umano, K.; Shibamoto, T.; *J. Agric. Food Chem.* **1987**, *35*, 909.
53. Yasuhara, A.; Shibamoto, T.; *Agric. Biol. Chem.* **1991**, *55*, 2639.

Submitted: February 19, 2013
Published online: September 27, 2013