

## Analytical, Nutritional and Clinical Methods

## Determination of acrylamide in potato chips by a reversed-phase LC–MS method based on a stable isotope dilution assay

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**Abstract**

Potato-based products represent an important part of the daily intake of food-derived acrylamide, mainly on adolescent population from western countries. A reversed-phase liquid chromatography-mass spectrometry based on a stable isotope dilution assay was used for acrylamide analysis. Aqueous sample extraction, cleaning with Carrez solution and solid phase extraction with methanol was applied. The ratio potato/NaCl solution is critical during extraction where the optimum ratio is 0.125 g/ml NaCl 2 M solution. The use of virgin olive oil, as retaining matrix, during methanol desiccation was critical to achieve high recoveries. The method performance was validated for limit of detection (23.2 µg/kg) and quantitation (91.8 µg/kg), linearity ( $r > 0.999$ , 25–1000 µg/kg), recovery (98.8%). The method was applied on commercial potato chips; the intra-day repeatability was set at 3.9% and values were corrected with a labeled internal standard ( $^{13}\text{C}_3$ -acrylamide). No significant differences on the acrylamide content were observed between industrial-scale and local-scale processed potato chips.

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**Keywords:** Acrylamide; Potato chips; Stable isotope dilution analysis; LC–MS**1. Introduction**

Acrylamide is a useful industrial chemical that was labeled as a probable human carcinogen by the International Agency for Research on Cancer (IARC). In this way, the contamination of drinking water or plants grown hydroponically has been the driving force in the past to develop methods for acrylamide monomer analysis (Castle, Campos, & Gilbert, 1991; Hashimoto, 1976). Things changed recently, when in April 2002, researchers from the University of Stockholm and the Swedish National Food Administration (NFA) reported the presence of acrylamide in a wide range of fried and oven-cooked foods, most notably in potato chips and French fries, at levels of 224–3700 µg/kg (Swedish Na-

tional Food Administration, 2002; Tareke, Rydberg, Karlsson, Eriksson, & Tornqvist, 2002). Besides, Mottram and Wedzicha (2002) showed how acrylamide could be formed from food components during heat treatment as a result of the Maillard reaction, likely asparagine and glucose. Asparagine, a major amino acid in potatoes and cereals, is a crucial participant in the formation of acrylamide by Maillard reaction at temperatures above 100 °C (Friedman, 2003). Since potato products are especially rich in asparagine and reducing sugars, it is now thought that this Maillard reaction is most likely responsible for the majority of the acrylamide found in potato chips and French fries.

The potential health risk of food acrylamide has been considered by number of government agencies and national authorities (Food Standards Agency, 2002; Scientific Committee on Food, 2002). Subsequently, all available data on acrylamide have been reviewed at international level, e.g., FAO, WHO, JIFSAN

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Workshop- identifying and listing a number of research gaps and priorities (FAO/WHO consultation, 2002; JIF-SAN, 2002). Among these, the development and validation of sensitive and reliable analytical methods for the quantification of acrylamide in different food matrices was considered as essential (Pittet, Périsset, & Oberson, 2004).

Because of its high water solubility and high reactivity (Motttram & Wedzicha, 2002) and also, because of the lack of a chromophore group, acrylamide is not easy to detect (Jezussek & Schieberle, 2003). At present, several analytical methods are available for determining acrylamide in foods and the majority are classical methods based on high performance liquid chromatography (LC) or gas chromatography (GC) techniques (Andrzejewski, Roach, Gay, & Musser, 2004; Barber, Hunt, LoPachin, & Ehrlich, 2001; Bologna, Andrews, Barvenik, Lentz, & Sojka, 1999; Castle, 1993; Jezussek & Schieberle, 2003; Kawata et al., 2001; Pittet et al., 2004; Tareke, Rydberg, Karlsson, Eriksson, & Törnqvist, 2000; Tekel, Farkas, & Kovác, 1989; US EPA, 1996). To increase the selectivity and also the sensitivity in GC analysis, bromination of the double bond in combination with electron capture detection was previously applied (Hashimoto, 1976); later, this method was improved by using either methacrylamide or *N,N*-dimethylacrylamide as internal standards and mass-spectrometry (MS) as detection method (Ahn et al., 2002; Jung, Choi, & Ju, 2003; Tareke et al., 2000; Tareke et al., 2002). However, several groups also described methods to quantify acrylamide by direct GC–MS measurements without bromination where the loss of acrylamide at the injection port should be evaluated (Biedermann, Biedermann-Brem, Noti, & Grob, 2002; Clarke, Kelly, & Wilson, 2002).

In a recent assessment of the performance of 37 laboratories in determining acrylamide in crisp bread, Clarke et al. (2002) reported that the majority of laboratories use either GC–MS or LC–MS with no obvious method-dependent differences in results obtained between the two approaches. However, the main advantage on LC–MS based methods is that acrylamide can be analyzed without prior derivatization, which considerably simplifies and expedites the analysis (Joint European Commission & Swedish National Administration, 2003). Many laboratories have developed its “own” LC–MS or LC–MS/MS technique (Andrzejewski et al., 2004; Ahn et al., 2002; Becalski, Lau, Lewis, & Seaman, 2003; Jezussek & Schieberle, 2003; Roach, Andrzejewski, Gay, Nortrup, & Musser, 2003; Tareke et al., 2002) but one of the limitations of these techniques is the difficulty of applying an universal clean-up approach valid for many different food matrices that avoid interferences from co-extractives (Presentation at HPLC, 2003).

The purpose of the following investigation was, therefore, to determine the acrylamide content of commercial

potato chips as a major source of acrylamide on the diet. In this way, a robust and sensitive LC–MS method was used taking into account different approaches described previously in the literature. Effectiveness of the procedure was evaluated and applied on the study of the content of acrylamide on potato chips.

## 2. Materials and methods

### 2.1. Samples

Experiments were conducted with a series of commercial potato chips (39 brands from 34 producers) randomly purchased on different supermarkets ( $n = 27$ ) and fried-potato shops ( $n = 12$ ). Samples (400–800 g) were thinly sliced to assure a homogeneous distribution of hot-spots. A portion (200 g) was distributed in four containers and stored under vacuum and light protected at 4 °C until analysis.

### 2.2. Chemicals and materials

[ $^{13}\text{C}_3$ ]-acrylamide (isotopic purity 99%) was from Cambridge Isotope Labs (Andover, MA, USA). Acrylamide (99%), potassium ferrocyanide (Carrez I), zinc acetate (Carrez II)-both analytical-reagent grade- and sodium chloride were from Sigma–Aldrich (St. Louis, MO, USA). Acetic acid (ultrapure grade) was from Merck (Darmstadt, Germany). Methanol and acetonitrile (HPLC grade) were from Scharlau (Barcelona, Spain).

The solid-phase extraction (SPE) cartridges Isolute Multimode (500 mg, 3 ml) were from IST (Hewgoed, Mid-Glamorgan, UK), reversed-phase Oasis HLB (200 mg, 6 ml) and mixed mode cation exchange cartridge Oasis MCX (60 mg, 3 ml) were from Waters (Milford, MA, USA). Syringe filter units (0.45  $\mu\text{m}$ , nylon) were purchased from Tecknokroma (Madrid, Spain).

### 2.3. Standard and reagents

Stock solutions of acrylamide (0.01 mg/ml) and [ $^{13}\text{C}_3$ ]-acrylamide (5  $\mu\text{g/ml}$ ) were prepared by dissolving the compounds in Milli-Q water and methanol, respectively. These solutions were then appropriately diluted with Milli-Q water (Millipore Corp., Madrid, Spain) to prepare working standards at 1.0  $\mu\text{g/ml}$ . All stock solutions and working standards were stored light-protected in a refrigerator at 4 °C for maximum 3 months. New working standards were compared with previous one as control of quality. Daily the instrument performance and relative response of labeled ( $m/z$  75.1) and unlabeled ( $m/z$  72.1) acrylamide was verified. Carrez I was prepared by dissolving 15 g of potassium ferrocyanide in 100 ml of water and Carrez II by dissolving 30 g of zinc acetate in 100 ml of water.

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