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**Determination of acrylamide in coffee and coffee products by GC-MS using an improved SPE clean-up**

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Table I.doc
Determination of acrylamide in coffee and coffee products by GC-MS using an improved SPE clean-up

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Abstract

An improved GC-MS method to determine acrylamide (AA) in coffee and coffee products was developed. The method was based in two main purification steps, the first one with ethanol and Carrez solutions in order to precipitate polysaccharides and proteins, respectively, and the second with a layered solid phase extraction (SPE) column which proved to be efficient to eliminate the main chromatographic interferences. The method is applicable to a wide range of coffee products. Twenty six samples of different coffee products were analysed. The levels of AA were in the range of 11.4 – 36.2 µg L⁻¹ for “espresso coffee” and 200.8 – 229.4 µg L⁻¹ for coffee blends with cereals. The results indicated that the presence of cereals significantly increased the levels of AA.

Keywords: Coffee, SPE clean up, acrylamide, GC-MS

Introduction
The occurrence of acrylamide (AA) in foodstuffs particularly in certain baked and fried products such as potato chips and French fries was first reported by Tareke et al. (2002). AA is now known to be formed by the Maillard reaction during industrial food processing, retail, catering and home food preparation ((Mottram et al., 2002; Stadler et al., 2002; Becalski et al., 2003)). The foodstuffs that contribute most to AA exposure vary depending upon the population’s nutritional habits and the way the food is prepared and processed (Dybing et al., 2005). Generally, the most important sources of AA appear to be potato products (potato chips, French fries, and potato snacks), cereals (breakfast cereals, roasted cereals), baked goods (bread, cookies, biscuits), and brewed coffee.

Recent reports showed that coffee is among the highest contributors to the AA intake in some countries in Europe. In Sweden the main dietary intake of AA from coffee was estimated to be 12 µg/day, representing ~39% of the total dietary intake of 31 µg/day (Svensson et al., 2003). These results were based on ready-to-drink coffee samples that contained around 25 µg kg\(^{-1}\) AA. Dybing and Sanner (2003) reported that a mean intake of AA from coffee was estimated to contribute to 28% of the 38 µg/day for males and 29% of the 29 µg/day for females in Norway. Their results were based on a study (Norwegian Food Control Authority, 2002) that reported concentrations of AA in filter coffee of 25 µg kg\(^{-1}\) and 10 µg kg\(^{-1}\) in instant coffee. A Swiss total diet study of AA in the diet of 14 men and 13 women showed that coffee contributed 36% of the total intake (Brunner et al., 2002). Granby and Fagt (2004) found in their study 2-16 µg L\(^{-1}\) of AA in brewed coffee and 10 µg L\(^{-1}\) AA in instant coffee. They concluded that the AA intake from coffee consumption in Denmark was 10 µg/day for males and 9 µg/day for
females. Assuming that the total exposure of Danish consumers is comparable to those of Sweden and Norway, the mean exposure to AA from coffee contributes to 20% of the total AA exposure. In Netherlands, Boon et al. (2005) accounted an AA concentration in coffee in the range 4 – 45 µg kg\(^{-1}\) that contributes with 13% of the total AA intake in adults. The US Food and Drug Administration (FDA) reported levels of AA in brewed coffee ranging from 6 to 16 µg L\(^{-1}\) (Andrzejewski et al., 2004).

In Portugal, coffee is highly consumed as “espresso” which has a peculiar brewing technique: a small amount of hot water (± 30 mL) is percolated in a very short time at high pressure through a layer of ground roasted coffee (± 6-7 g), the coffee cake, to produce efficiently a very concentrated brew (≈200 g of ground coffee per litre) comparing with the 20 – 60 g of ground coffee per litre related in the above mentioned countries (Nunes & Coimbra, 1987).

Several methods to determine AA in food have been developed and they are based on either GC-MS with derivatisation with bromine (Andrawes et al., 1987; Nemoto et al., 2002; Ono et al., 2003; Pittet et al., 2004) and without derivatisation (Jezussek & Schieberle, 2003; Biedermann et al., 2002; Amrein et al., 2005) or LC-MS with derivatisation with mercaptobenzoic acid (Jezussek & Schieberle, 2003) and without derivatisation (Roach et al, 2003; Becalski et al., 2003; Ahn et al., 2002; Rosén et al., 2002; Şenyuva & Gökmen, 2005 & 2006; Delatour et al., 2004; Andrzejewski et al., 2004; Yusà et al., 2006). Independently of the chromatographic technique adopted, the success of the methods is very dependent of the extraction and clean-up steps. The most used procedures usually fail when dealing with coffee products, due to their inability to
avoid the presence of interferences that co-elute with the analyte thus preventing its correct quantification (Delatour et al., 2004).

The methods developed so far to determine AA in coffee and coffee products, are based mainly in LC-MS/MS with variations in the clean-up conditions employed. Roach et al. (2003) used a combination of Oasis HLB and Bond Elut-Accucat SPE cartridges before the LC analysis but found coffee to be a troublesome matrix. The method still presents some problems regarding contaminations, as it requires frequently reconditioning the HPLC column (Andrzejewski et al., 2004). Granby and Fagt (2004) performed a single-step clean-up on 300 mg Isolute Multimode SPE columns of five hundreds microlitres of sample to make the clean-up more efficient and eliminate almost completely the colour from the coffee. However, they referred that the loading of the SPE cartridge with the sample exceeding 0.5 mL resulted in a suppression of the MS response. Şenyuva and Gökmen (2005) extracted AA from ground coffee using methanol instead of water and the clean-up was made with Oasis HLB SPE cartridges prior to LC analysis. Delatour et al. (2004) used 500 mg of Isolute Multimode SPE cartridges to clean-up 2 mL of samples but realized that a single step was not effective and developed a combination of liquid-liquid and solid phase extraction methods. Ono et al. (2003) determined acrylamide in several food items including roasted coffee by GC-MS. However no reference was made about the efficiency of their method to coffee analysis. The set of methods developed so far demonstrate a lack in the methodologies employing GC-MS with the objective to specifically determine AA in coffee samples.
The objective of this work was to develop a method to determine AA in several coffee products using GC-MS as analytical technique. The method was successfully applied to determine acrylamide in ready-to-drink products and ground coffee, that was analysed as “espresso”.

**Experimental**

**Sampling and coffee preparation**

Eighteen samples of roasted coffee beans, five samples of instant coffee, two of them decaffeinated, two samples of coffee blends with cereals and one soluble “cappuccino” were collected from several supermarkets and stored at room temperature. The most common brands were selected. The roasted coffee beans were ground in a coffee grinder incorporated in a Philips coffee machine, model Espresso Professional selected for a fine grain size typical for espresso coffee preparation. Each espresso was prepared in duplicate according to the typical conditions used in Portugal for an “espresso” preparation, i.e.: 7 g of ground coffee extracted with hot water during 30 ± 5 s (about 30 to 35 mL of water) at an inlet pressure of 9 ± 2 bar. Two grams of instant coffee, coffee blends and cappuccino were dissolved in 10 mL of deionised water.

**Chemicals**

Acrylamide (AA) 99% purity grade was acquired from Aldrich (Steinheim, Germany).

Acrylamide 1,2,3-C13 (13C3-AA) 99% in methanol was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). The solid-phase extraction (SPE) columns, Isolute Multimode, 3 g custom made, were from International Sorbent Technology (Hengoed, Mid Glamorgan, UK). The preparative C18 sorbent 125 Å, 55-105 μm was
from Waters (Milford, USA). The filters were polyethylene single fritted reservoir 25 mL, filter pore size 10 µm (Symta, Madrid, Spain). The n-hexane and ethyl-acetate were of pesticide residue analysis grade and methanol and acetonitrile were of ultrapure grade, all from Fluka. The potassium bromide for IR spectroscopy grade and the bromine analytical grade were from Merck (Darmstad, Germany). Sodium chloride analytical grade was from J.T. Baker (Deventer, Holland). Potassium hexacyanoferrate (II) trihydrate, zinc sulphate heptahydrate, acetic acid (glacial) and absolute ethanol were analytical grade obtained from Panreac (Barcelona, Spain). Hydrobromic acid 48% and sodium tiosulphate volumetric solution 1 mol L\(^{-1}\) were from Riedel-de Häen (Seelze, Germany).

Standards and reagents

A stock solution of AA (2 g L\(^{-1}\)) was prepared by dissolving the compound in acetonitrile, and appropriately diluted to prepare a working standard solution at 4 mg L\(^{-1}\). A stock solution of internal standard, \(^{13}\)C\(_3\)-AA, was prepared by the same way with the difference that the working standard solution was made at 40 mg L\(^{-1}\). All stock and working solutions were stored at 4°C. Saturated bromine water solution and Carrez reagents were prepared according to Pittet et al. (2004).

Sample preparation

To 10 mL of “espresso” coffee or 2 g of other coffee product dissolved in 10 mL of water, 15 mL of absolute ethanol were added and the solution shaken for ~ 1 min. 0.5 µg of IS was added and the solution was shaken again and then kept at -20°C during 15 minutes. It was centrifuged at 15000 g (5 minutes, 4°C) and the resulting solution was
transferred to a centrifugal flask. Afterwards, it was acidified with acetic acid until pH 4-5 (0.1-0.2 mL). 1 mL of Carrez I and 1 mL of Carrez II solutions were added and then the flask shaken and kept at 4 ºC for 15 minutes. The solution was centrifuged at 15000 g (15 minutes, 4ºC) and filtrated to a 40 mL vial through the polyethylene filters. The volume of the solution was reduced to 2-3 mL in a rotary evaporator at 55ºC and transferred to a 20 mL vial. The rotary evaporator vessel was washed with 2 mL of water that was added to the solution in the vial. If necessary a centrifugation at 3000 g was performed to deposit suspended solids in the solution prior to the SPE clean-up.

SPE clean-up

The SPE columns were prepared by adding a 1g layer of C18 sorbent to the Isolute Multimode 3 g column. This layer was covered with a polyethylene frit (pore size 10 µm). The columns were conditioned first with 20 mL of methanol and then with 20 mL of water. The sample solution (~5 mL) was loaded on the column and the first 2 mL of the eluate were discarded. The remaining solution (~3 mL) was collected in a 40 mL vial and the column was washed with 10 mL of water that was collected to the same vial.

For instant coffee it was necessary to perform a previous SPE cleaning with a 3g C18 columns home made prior to the Isolute cleaning. The column was conditioned under the same conditions as the Isolute column and the sample was loaded and eluted with just 1 mL of water. This solution was collected and loaded in the prepared Isolute columns.
Bromination

To the collected extract 1 g of calcinated KBr was added. The solution was then acidified with HBr until pH 1-3 (100-150 µL) and 2 mL of saturated bromine solution were added. The solution was allowed to stand in an ice bath and kept from the light at least during 1 h. The excess bromine in the solution was decomposed by the addition of 1 mol L\(^{-1}\) sodium tiossulphate until the yellow colour disappeared (50-150 µL). The extract was saturated with 4 g of NaCl and extracted twice with 10 mL and 5 mL portions of ethyl acetate/n-hexane 4:1 (v/v). The volume was reduced to 3 mL under a stream of nitrogen and a small quantity of anhydrous Na\(_2\)SO\(_4\) was added. Finally, the solution was centrifuged at 3000 rpm during 3 min, the upper layer was transferred to another vial and evaporated to 0.5 mL under a gentle stream of nitrogen. The solutions were then injected in the gas-chromatograph.

Calibration standard

Aliquots of the working standard AA solution (equivalent to 0 to 3 µg of AA corresponding to 0 to 300 µg L\(^{-1}\) in the samples) were taken into 50 mL centrifugal tubes and 0.5 µg of internal standard was added to each tube and made up to 10 mL with water. These solutions were treated according to the overall procedure (clean-up included) described for the samples.

Equipment

GC-MS analysis were performed in a gas-chromatograph, model HP GC-6890, split-splitless injector, coupled to a Mass Selective Detector model Agilent MSD-5973N (Agilent, Palo Alto, CA, USA). The analytical separation was performed in a capillary
column DB 1301 (30 m x 0.25 µm, 0.25 mm i.d.) from J&W Scientific (Folsom, CA, USA). The centrifugations were made in an ultra-centrifuge from Eppendorf, model 5810 R (Hamburg, Germany) at 15000 g and in a Heraeus Sepatek, model Labofuge Ae (Osterode, Germany) at 3000 g. The SPE clean-up was made in a Visiprep Solid Phase Extraction Manifold from Supelco (Taufkirchen, Germany) with capacity for 12 columns. Evaporation of the solvents was performed in a Büchi Rotavapor model RE 111 and 461 water bath (Flawil, Switzerland). The evaporation under a stream of nitrogen was carried out on a Pierce, model Reacti-therm 18790 (Rockford, IL, USA) with capacity for 9 vials.

GC-MS Operating conditions

Gas-chromatography. Carrier gas: helium (constant flow at 1 mL min⁻¹). Sample injection volume: 1 µL (splitless, pulsed pressure 32 psi, 60 sec). Injector temperature: 280 ºC. Oven temperature: 85ºC (1 min), 15ºC min⁻¹ to 280ºC, hold 10 min (24 min), transfer line, 240 ºC.

Mass-spectrometry. Electron energy, 70 eV (EI mode). Mode of acquisition: selected ion monitoring (SIM), m/z 106, 108, 150 and 152 for 2,3-dibromopropionamide (2,3-DBPA) and m/z 110, 153, 155 for 2,3-¹³C₃- dibromopropionamide (2,3-¹³C₃-DBPA). The ions m/z 150 for 2,3-DBPA, m/z 155 for 2,3-DBPA(¹⁵C₃) were used for quantification and the others for confirmation. AA was determined with the internal standard using the ratio of peak area of 2,3-DBPA to 2,3-¹³C₃-DBPA. The identity of the peak was confirmed by retention time and by comparing the relative abundance ratios of the confirmatory ions with those of standard solution.
Results and discussion

Method development

Aiming for screening of the presence of AA in food products largely consumed in Portugal, we developed a GC-MS methodology (not published) based on the several papers published in this field (Tareke et al., 2002; Nemoto et al., 2002; Ono et al., 2003; Pittet et al., 2004; Biedermann et al., 2002; Delatour et al., 2004). Briefly, AA was extracted from the samples with water at 65 °C, Carrez solutions were added in order to precipitate proteins, the upper layer partially evaporated and finally the compound was brominated, extracted twice by ethyl acetate:n-hexane 4:1 (v/v) and then analysed by GC-MS in SIM mode.

As reported by other authors (Delatour et al., 2004; Andrzejewski et al., 2004) that used similar methods, some drawback occurred when difficult matrices were analysed, namely coffee products. Taking this into account some modifications were introduced in our previous developed method.

The addition of absolute ethanol to coffee samples intended to control the great quantity of foam that was constantly being formed during almost all steps of the sample preparation and resulting in severe losses of the analyte and contamination of the used instruments. The problem was particularly serious during the evaporation step on the rotary evaporator because the foam was always being projected. The adopted solution was an adaptation from the work of Nunes and Coimbra (1998), where the precipitation of polymeric polysaccharides, responsible for the “foam stability” in espresso coffees, was achieved by adding 55 and 75 % ethanol solution at 4°C during one hour. After
trials with 5, 10, 15, 20, 25 mL of ethanol, 15 mL were found to give the best results.

The precipitation time was decreased to 15 minutes by changing the precipitation temperature from 4ºC to -20ºC.

The SPE clean-up was a challenge in the sense that it was difficult to achieve the correct ratio between the two used sorbents. The use of a single purification step with C18 revealed to be useful to eliminate the coffee colour but it was not effective to remove other compounds that overlapped the 2,3-DBPA peak no matter what quantity of sorbent was used. When using Isolute Multimode cartridges (0.5 or 1 g) it was verified that the sorbent layer was completely saturated with very small quantities of coffee samples (0.5-1.0 ml). Because it was difficult to achieve such small sample volumes during the evaporation step, the rejection of an important portion of the extract was necessary, with the inherent loss of sensitivity of the overall method. The solution found was to increase the quantity of sorbent material instead of decreasing the sample volume. The use of higher quantities of Isolute Multimode (3g) resulted in an increase of the analytical signal but it was not effective to eliminate the coloured compounds and suppression of the MS response was observed. The addition of both sorbents in a single step was the solution found to surpass both problems. It was found that a ratio of 1:3 of C18: Isolute was ideal to eliminate the most relevant contaminants present in “espresso” coffee.

Soluble coffees, revealed to be a troublesome matrix due to its high percentage of concentrated polysaccharides. The addition of ethanol was not enough to eliminate the majority of the polysaccharides that increased the formation of foam and the 1:3 ratio...
between the sorbents was incapable of eliminate all the interferences observed in the analytical signal. Besides, these samples provoked contamination of the injector, what demanded constant changing of the liner sometimes just after few injections. The addition of a bigger top layer of C$_{18}$ was impracticable due to the dimensions of the used cartridges. The use of a previous clean-up step with a C$_{18}$ sorbent, in which the majority of the coloured compounds were eliminated, followed by a second clean-up step with the “C$_{18}$ layered” Isolute column was the best solution found. Notwithstanding the slight decrease observed in the analytical signal, the use of a “clean” extract provided a much better quality of the chromatographic results.

The analytical separation of acrylamide was performed in a DB 1301 capillary column. In Figure 1 is presented a chromatogram for an “espresso” coffee sample with 20.8 µg L$^{-1}$ AA and 0.5 µg $^{13}$C$_3$-AA corresponding 50 µg L$^{-1}$ in the sample.

[Insert Figure 1 about here]

Method assessment

Linearity. The linearity of the method was tested several times using standard (calibrating) solutions performed in water and treated using the same method developed for the samples. Six standards were simultaneously prepared and treated in parallel with the sample. The range of concentrations varied according to the expected levels of AA in coffee samples. Typical ranges were 0-300 µg L$^{-1}$ AA in the sample. The quantity of IS was 0.5 µg corresponding to 50 µg L$^{-1}$ in the sample for all samples and standards.
Calibration curves were constructed by plotting the AA/IS area ratio against the concentration of AA in the standard. The correlation coefficients were usually higher than 0.997.

**Precision.** To study the precision of the method, an "espresso" coffee (~30 mL) was divided in three aliquots of 10 mL each, which were submitted to the overall developed method and injected twice. The RSD obtained was 6.3%.

**Recovery.** For the recovery test, an instant coffee surrogate solution (containing 200.8 µg L\(^{-1}\) of AA) was prepared with 8 g of powder dissolved in 40 mL of water and divided into four aliquots of 10 mL each. AA was added at each aliquot at the levels from 0 to 2 µg corresponding to 0-200 µg L\(^{-1}\). After addition of IS the samples were analysed by the described overall method. The AA recovery from the spiked solutions varied between 97.4 to 108.4%.

**Limit of detection and limit of quantification**

No exhaustive studies for determining the limit of detection were made. However, standards containing 10 µg L\(^{-1}\) of AA, were used to construct the calibration curves. Under conditions of ideal performance of the MS detector, it was possible to integrate the corresponding peaks of AA and for the IS. Replicate analysis (extraction procedure included) of these standards showed that the values obtained for the ratio area of AA/IS, presented a R.S.D. less than 15%. This fact was confirmed when samples containing very low levels of AA were analysed. For example, a sample of Espresso coffee containing 20.5 µg L\(^{-1}\) of AA was analysed in triplicate ant the RSD obtained was 13.6
%. Below this level of concentration the values obtained registered an R.S.D. above 15%.

Method application

The method developed was applied to 26 coffee samples (roasted beans, instant and coffee blends). Samples were randomly selected from supermarkets, and therefore may not be representative of coffee supply. Nevertheless they represent a general guide to AA concentration in a selected segment of coffee supply. The results obtained are presented in Table I. Accordingly AA levels ranged from 11.4 to 36.2 µg L⁻¹ in ground roasted coffee analysed as “espresso”, 47.4 to 95.2 µg L⁻¹ for instant coffee and 200.8 to 229.4 µg L⁻¹ for coffee blends with cereals. Soluble “cappuccino” contained 6.4 µg L⁻¹.

Considering that 6 g of ground coffee extracted with ~30 mL water are used to prepare an “espresso”, the concentration of AA per cup is therefore 0.32 to 1.46 µg/30 mL. To prepare a cup of instant coffee the usual measure is 2 g per individual portion making 0.47 to 0.95 µg per 30 mL. Considering that coffee blends with cereals were prepared as soluble coffee (2 g/30 mL cup) the concentration of AA per cup is therefore 2.01 to 2.09 µg per 30 mL cup. “Cappuccino” as analysed is a soluble mixture of coffee, milk powder, cocoa and sugar and each individual dose correspond to 14 g, resulting in an AA concentration of 0.45 µg per 30 mL cup. These results highlight the fact that the addition of cereal products to coffee increased the amount of AA. This is in agreement with studies (Yusà et al., 2006) reporting that cereal products form substantial amounts of AA due to their chemical constitution and processing.

[Insert Table I about here]
Conclusion

To date, LC/MS has been the most widely used analytical approach to assay AA in coffee. GC/MS methods usually suffer from the presence of co-extractives which rapidly contaminate the chromatographic system, degrading the respective performance and avoiding the correct quantification of AA. This paper describes a GC/MS method based on an improved sample preparation procedure that enables the correct quantification of AA in coffee extracts without the problems generally associated with those kind of samples. The high levels of sensitivity, and reproducibility achieved recommend it when dealing with this type of food matrices. The method was applied to several coffee products and the quantity of AA was found to be dependent on the coffee processing and preparation, namely the addition of cereals.

Acknowledgements

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References


Figure 1. Chromatogram of a ground coffee sample analysed as “espresso” coffee with 20.8 µg L\(^{-1}\) AA and addition of 0.5 µg of \({}^{13}\)C\(_3\)-AA corresponding to a concentration of 50 µg L\(^{-1}\) AA. \(m/z\) 150 is the quantification ion for AA and ion \(m/z\) 155 is the quantification ion for \({}^{13}\)C\(_3\)-AA.
Table I. Acrylamide levels measured in 26 coffee products. The minimum and maximum values are presented and also the mean level of AA in the different coffee products analysed.

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