Abstract

Mass Transfer of Dichloromethane from EU Retail Roast and Ground Decaffeinated Coffee into Prepared Beverages †

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**Abstract:** Dichloromethane (DCM) is extensively used around the globe in various applications, such as in closed industrial installations for food processing or pharmaceutical extractions (vitamins, antibiotics, etc.). In the coffee sector it is used as an extraction agent for the decaffeination process of green coffee beans. Due to its low boiling point, ranging at approx. 40°C, DCM can be easily removed subsequent to caffeine extraction by applying state of the art solvent stripping processes. The intention of this study is to assess how much DCM, if any, is present in decaffeinated coffee packages as sold to the consumer, as well as how much of the extraction solvent residue is transferred into the finally prepared, consumable coffee beverage. This study sets out to highlight DCM contents of decaf coffees, directly taken from 6 EU countries’ supermarket shelves. In addition, DCM mass transfer rates from roasted coffee matrices into the corresponding, variously prepared beverages (drip percolated coffee, French press) are determined. All analyses were performed applying a Headspace-GC-MS technique. All presented data demonstrate that DCM residues in the 34 coffee samples analyzed have contents well below the DCM maximum residue limits for roasted coffee both in the European Union (2 mg/kg) and the USA (10 mg/kg), with an average of 0.127 mg/kg, median value of 0.059 mg/kg and P95 of 0.444 mg/kg. Furthermore, this study shows that DCM mass transfer rates from the coffee matrices into the corresponding beverages have for drip coffee an average of 24.7%, median of 26.8% and for French press average mass transfer of 41.9%, median of 43.1%.

**Keywords:** dichloromethane; decaffeination; roasted coffee; drip coffee; French press

1. Introduction

The intention of this study is to review how much dichloromethane (DCM) is present in decaffeinated coffee consumer packages when DCM was used as extraction solvent and how much is actually transferred to beverages as consumed.

For the decaffeination process of green coffee dichloromethane is used around the globe extensively as an extracting agent, where the solvent is in direct contact with the green coffee beans. Due to its low boiling point, dichloromethane can be easily removed after caffeine extraction by vaporization. To prevent any risk to human health, maximum residue levels of dichloromethane in roasted coffee were set in Europe and the US.

This study analyses the DCM content of coffees provided to the consumer and compares the transfer from roasted coffee into two differently brewed beverages, drip coffee and French press, respectively.

2. Materials and methods

2.1 Coffee samples

The samples to be analysed for dichloromethane were 34 different commercially available roasted decaffeinated coffee products. 26 samples were decaffeinated roasted and ground coffee, three samples decaffeinated and roasted whole coffee beans and three samples decaffeinated, roasted and ground coffee in capsules.

All 34 samples were brewed as drip coffee and in a French press. Samples of all preparations were analysed on dichloromethane directly after beverage preparation.

For the analysis of Dichloromethane, the following equipment was used: Agilent headspace gas chromatograph 7890 with MSD 5977 A, Gertel MPS 2 autosampler and cold injection system KAS 4 with Carbotrap liner. Chromatographic column: J&W PoraPlot Q 25 m x 0.32 mm ID, 0.45 µm film and carrier gas was Helium.

2.5 g coffee powder or 10 mL brew sample was transferred into a 20 mL headspace vial. Coffee powder was covered with 10 mL purified water. Incubation time for the vial was 10 min at 80 °C. Injection volume was 2.0 mL gas sample in solvent venting mode. Quantification was done using an external 6 point matrix calibration with dichloromethane standard (LGC). DCM was identified and quantified at m/z 84 and 86 respectively in ESI positive SIM mode.

2.2. Coffee beverage preparation

The three samples of roasted whole beans were ground with a Mahlkoenig® EK43S coffee mill with typical medium coarseness required for the subsequent extraction.

For the brewing preparation of the three samples of capsules, the capsules were opened and the content of ten capsules of each sample was mixed and used for the extraction.

2.3 Preparation of drip coffee

Filter drip coffee preparation was performed manually with a V60 dripper. The V60 coffee filter paper was rinsed with hot water and 20 g ground (medium coarseness) coffee powder was weighed into the filter. The ground coffee was moistened with 90-95°C hot water until it was completely covered and simmered for about 30 seconds. In circular motions the remaining of total 300 g hot water is poured on top. If necessary, the filter was stirred briefly. After the extract had completely drained through the coffee bed, the beverage sample flask was directly closed and analysed.

2.4 Preparation of coffee in the French press

For the preparation of coffee samples in the French press 20 g of coffee powder were directly weighed into the French press and poured over with 300 g of hot water (90-95°C). The extract was stirred briefly, and the lid was lightly pressed on the surface, so that the coffee powder was completely covered with water. After approx. three minutes the lid was pressed down slowly and evenly. The freshly prepared coffee was directly filled in a sample flask and analysed.

3. Results

**DCM in original R&G coffee samples**

The 34 original R&G coffee samples have concentrations ranging from 5.7 to 816.6 µg/kg (Fig. 1), with an average of 127 µg/kg, median value of 59.5 µg/kg and P95 of 443.6 µg/kg.

Figure 1: DCM concentration in original R&G coffee samples in µg/kg

**DCM content per portion and transfer rate in the beverage**

Based on the results above, the DCM content per portion in original R&G Coffee samples (20 g) was calculated and the results compared with the content per portion in drip coffee (0.3 L) and French press (0.3 L), as resumed in Table 1; then, the transfer rates were calculated and reported both in Table 1:

Table 1: DCM content per portion original R&G Coffee sample (20 g), drip coffee (0.3 L) and French press (0.3 L) and transfer rate in the beverage:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Sample** | **Sample type** | **original R&G coffee** | **drip coffee** | | **French press** | |
| **m(DCM) [µg]** | **m(DCM) [µg]** | **DCM transfer** | **m(DCM) [µg]** | **DCM transfer** |
| **in 20g portion** | **in 0,3L portion** | **[%]** | **in 0,3L portion** | **[%]** |
| R&G 01 | R&G Coffee, decaf | 1.47 | 0.315 | 21.4 | 0.519 | 35.3 |
| R&G 02 | R&G Coffee, decaf | 0.75 | 0.094 | 12.5 | 0.191 | 25.5 |
| R&G 03 | R&G Coffee, decaf | 1.19 | 0.273 | 23.1 | 0.336 | 28.3 |
| R&G 04 | R&G Coffee, decaf | 0.41 | <0,075 | 0.0 | <0,075 | 0.0 |
| R&G 05 | R&G Coffee, decaf | 1.99 | 0.577 | 29.0 | 0.845 | 42.4 |
| R&G 06 | R&G Coffee, 50% Caffeine | 1.20 | 0.214 | 17.9 | 0.344 | 28.8 |
| R&G 07 | R&G Coffee, decaf | 1.75 | 0.464 | 26.5 | 0.626 | 35.8 |
| R&G 08 | R&G Coffee, decaf | 1.99 | 0.659 | 33.1 | 0.906 | 45.6 |
| R&G 09 | R&G Coffee, decaf | 1.03 | 0.238 | 23.1 | 0.472 | 45.8 |
| R&G 10 | R&G Coffee, decaf | 1.10 | 0.294 | 26.7 | 0.448 | 40.7 |
| R&G 11 | R&G Coffee, decaf | 2.39 | 0.714 | 29.9 | 0.956 | 40.1 |
| R&G 12 | R&G Coffee, decaf | 1.02 | 0.235 | 22.9 | 0.398 | 38.9 |
| R&G 13 | R&G Coffee, decaf | 6.66 | 2.024 | 30.4 | 4.985 | 74.9 |
| R&G 14 | R&G Coffee, decaf | 5.18 | 3.080 | 59.4 | 5.246 | 101.2 |
| R&G 15 | R&G Coffee, decaf | 5.15 | 2.213 | 43.0 | 4.011 | 77.9 |
| R&G 16 | R&G Coffee, decaf | 0.84 | 0.230 | 27.3 | 0.387 | 45.8 |
| R&G 17 | R&G Coffee, decaf | 0.79 | 0.099 | 12.6 | 0.252 | 32.1 |
| R&G 18 | R&G Coffee, decaf | 0.58 | <0,075 | 0.0 | 0.102 | 17.5 |
| R&G 19 | R&G Coffee, decaf | 3.83 | 1.029 | 26.9 | 1.880 | 49.1 |
| R&G 20 | R&G Coffee, decaf | 4.21 | 1.008 | 23.9 | 2.103 | 50.0 |
| R&G 21 | R&G Coffee, decaf | 0.38 | <0,075 | 0.0 | 0.125 | 32.4 |
| R&G 22 | R&G Coffee, decaf | 0.93 | 0.341 | 36.7 | 0.560 | 60.2 |
| R&G 23 | R&G Coffee, decaf | 0.84 | 0.234 | 27.8 | 0.401 | 47.6 |
| R&G 24 | R&G Coffee, decaf | 0.36 | <0,075 | 0.0 | <0,075 | 0.0 |
| R&G 25 | R&G Coffee, decaf | 16.33 | 6.345 | 38.9 | 9.053 | 55.4 |
| R&G 26 | R&G Coffee, decaf | 1.28 | 0.378 | 29.4 | 0.600 | 46.7 |
| R&G 27 | R&G Coffee, decaf | 1.00 | 0.362 | 36.3 | 0.438 | 43.9 |
| R&G 28 | R&G Coffee, decaf | 2.60 | 1.131 | 43.5 | 1.296 | 49.8 |
| RWB 01 | roasted, whole beans, decaf | 1.30 | 0.307 | 23.7 | 0.449 | 34.6 |
| RWB 02 | roasted, whole beans, decaf | 0.93 | 0.294 | 31.6 | 0.496 | 53.2 |
| RWB 03 | roasted, whole beans, decaf | 3.07 | 1.111 | 36.2 | 1.743 | 56.9 |
| Cap 01 | R&G Coffee Capsules, decaf | 0.11 | <0,075 | 0.0 | <0,075 | 0.0 |
| Cap 02 | R&G Coffee Capsules, decaf | 12.99 | 6.050 | 46.6 | 11.454 | 88.2 |
| Cap 03 | R&G Coffee Capsules, decaf | 0.83 | <0,075 | 0.0 | <0,075 | 0.0 |
|  |  |  |  |  |  |  |
|  | **Average** | 2.54 | 1.08 | 24.71 | 1.72 | 41.90 |
|  | **Median** | 1.19 | 0.37 | 26.79 | 0.54 | 43.14 |
|  | **P95** | 8.87 | 5.01 | 44.59 | 7.34 | 81.50 |

4. Conclusions

The data presented show that DCM residues in the 34 samples analysed, directly taken from 6 EU countries’ supermarket shelves, have contents well below the DCM maximum residue limit for roasted coffee in EU (2 mg/kg) or USA (10 mg/kg), with an average of 0.127 mg/kg, median value of 0.059 mg/kg and P95 of 0.444 mg/kg.

Furthermore, this study shows that DCM mass transfer rates from the coffee matrices into the corresponding beverages have for drip coffee an average of 24.7% (median of 26.8%) and for French press average mass transfer of 41.9% (median of 43.1%), demonstrating that the brewing process contributes to a further reduction of the DCM content in the beverage.

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**Conflicts of Interest:** M.F. is the owner, President and CEO of Demus S.p.A., O.S.-H. is CEO of CR3-Analytik GmbH & Co. KG, a company of the Hermsen Group, G.M. is Head of Product Research of Coffein Compagnie GmbH & Co. KG. Among other activities, all three companies operate on green coffee decaffeination. J.H. is CEO for Deutscher Kaffeeverband, the German Coffee Association.

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