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Analysis of migration of polyfluorinated compounds from paper packaging into food matrices

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Introduction. Polyfluorinated compounds are extensively utilized as grease- and water repellants in paper- and cardboard used as food contact materials. These bioaccumulative substances are able to migrate from the food contact material into foods. In this study, we compare two extraction methods for polyfluorinated compounds in food samples; liquid-liquid extraction by trifluoroethanol and methanol extraction/saponification/weak ion exchange solid phase clean-up.

Materials and methods. Two food products; popcorn and flour, were extracted with LLE [1] and with SPE [2]. Extraction scheme for the SPE method is presented in Figure 1. LLE was performed by a two-phase system where 0.2 g food product was extracted by 5 mL of isooctane and 2 mL 80:20 (v/v) trifluoroethanol and water. Products were simulated for storage and usage and pre-treated according to Table 1.

The compounds analysed were polyfluorinated mono- and di-aryl phosphate esters (mono-PAPs, di-PAPs, and S-di-PAPs). The analysis was performed by HPLC-MS-MS for the SPE method or by UHPLC-MS-MS for the LLE technique. Ct1-labelling standards were used as internal standards.

Table 1. Pre-analysis treatment of food products and food simulants.

<table>
<thead>
<tr>
<th>Food product</th>
<th>Storage simulation</th>
<th>Usage simulation</th>
<th>Pre-treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Popcorn</td>
<td>NA</td>
<td>Popped</td>
<td>Cryomorphogenised, saponificated*</td>
</tr>
<tr>
<td>Fluor</td>
<td>40 °C, 10 days</td>
<td>NA</td>
<td>Saponificated</td>
</tr>
</tbody>
</table>

1-2 g food sample
18 mL methanol
Shaken overnight

Centrifugation:5 min, 3100 rpm, 5°C
HPLC-MS-MS

Table 4. Mean recovery and relative standard deviation for spiked flour (500 ng/g) extracted by the SPE method.

<table>
<thead>
<tr>
<th>Compound/ Sample</th>
<th>4:2 mono-PAP</th>
<th>6:2 mono-PAP</th>
<th>8:2 mono-PAP</th>
<th>10:2 mono-PAP</th>
<th>4:2 di-PAP</th>
<th>6:2 di-PAP</th>
<th>8:2 di-PAP</th>
<th>10:2 di-PAP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean recovery (%)</td>
<td>65</td>
<td>54</td>
<td>101</td>
<td>8</td>
<td>67</td>
<td>56</td>
<td>64</td>
<td>51</td>
</tr>
<tr>
<td>Relative std (%)</td>
<td>9</td>
<td>6</td>
<td>54</td>
<td>61</td>
<td>20</td>
<td>20</td>
<td>22</td>
<td>22</td>
</tr>
</tbody>
</table>

Ph: 3.5 (formic acid)
Oasis Wax SPE 150 mg, 30 μL
Elution: 6 mL 1% NH4OH in methanol
20 mL KOH; overnight

Figure 1. Extraction scheme for the methanol extraction/saponification/weak ion exchange solid phase clean-up. The SPE clean-up were performed according to the manufacturer’s protocol.

Results and Discussion. Since 2010, it is recommended by the European Council, to monitor mono- and di-PAPs in food products. We have compared the two most common extraction strategies for per- and polyfluorinated compounds used for food products.

Test for the extraction efficiency of migrated fluorinated compounds into food products:

- The trifluoroethanol extraction method revealed high recovery for for mono-PAPs and di-PAPs. This method included internal standards of 6:2 mono-PAPs, 8:2 mono-PAPs, 6:2 di-PAPs and 8:2 di-PAPs. The recoveries of 4:2 mono-PAPs and 4:2/4:2 di-PAPs are insufficient, probably due to degradation of these compounds in the non-commercial standard. All other standards used were commercially obtained.
- On the contrary the SPE method only included 6:2 di-PAPs as internal standard. The recovery was fair for the 6:2 di-PAPs but it is evident that the accuracy is not adequate for some of the other compounds. However, omitting the internal standard resulted in too low recoveries. Including more internal standards is essential for better accuracy and precision. Therefore, further analysis is necessary to validate this method.

Conclusion. The liquid-liquid extraction provides a simple, and efficient method for the extraction of mono- and di-PAPs in food matrices relevant for surveying potential migrating fluorinated compounds from food contact materials. The SPE method, which have good recoveries for PFCs (data not shown), had relatively poor accuracy. This study further emphasizes the necessity for using compound specific internal standards, preferable for each analyte.
