Identification and semi-quantification of known and novel contaminants in indoor dust by ion-mobility high-resolution mass spectrometry and estimation of risks for human exposure

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INTRODUCTION

- Dust is important for exposure since humans spend 80% of their time indoors
- Toddlers are a highly exposed risk group due to hand-to-mouth contact
- Dust functions as a sink of indoor contaminants which has been underlined by the results of quantification studies on several classes of contaminants
- Due to the ever-evolving chemical exposure there is a complementary need for the identification of contaminants of emerging concern (CECs)
- Screening of 46 Flemish dust samples from houses, offices, and leisure venues
- Drift tube ion-mobility (IM) mass spectrometry (MS) was applied as an additional separation dimension to liquid chromatography (LC) and high-resolution mass spectrometry (HRMS)
- IM-MS allows for the calculation of collision cross-section values (CCS) to further increase identification confidence.

MATERIALS AND METHODS

Sample Preparation

- 20 mg dust (25-50 μm)
- Spoke internal standards 0.1-0.5 μg
- 2x2.5 mL n-Hexane/Acetone 0.5 mL Toluene
- GC-QqQ data not included

Instrumentation

- Agilent 6560 HPLC-IM- QTOF
- Column: InfinityLab Poroshell 120 EC-C18
- ESI+ (A) H2O + 0.3% FA
- (B) MeOH + 0.1% FA
- Mass range: m/z 100-1500
- Acquisition: QTOF only – data dependent acquisition and IM-MS 4bit multiplexing
- Software: Mass Profiler Professional, Agilent MassHunter, IM Browser

Data Processing

- QC and IS
  - RT stability - mass accuracy – stable signal intensities
  - Target screening with in-house standards
  - Suspect list with known and novel CECs (n > 4000)
- IM-MS analysis
  - CCS values for all compounds
  - [M+H]/[M+Na]+ adducts
  - Match with established database (CCS < 2%) and m/z
  - Comparison with m/z-CCS trends

RESULTS

Phthalate identification

<table>
<thead>
<tr>
<th>Compound</th>
<th>DF (%)</th>
<th>CL</th>
<th>Estimated Conc. (µg/g)</th>
<th>EDI (mg/kg bw/day)</th>
<th>HQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diisodicyl phthalate (DIDP)</td>
<td>97.8</td>
<td>CL 1</td>
<td>3.2-90</td>
<td>5.71±0.5</td>
<td>-</td>
</tr>
<tr>
<td>Diisononyl phthalate (DINP)</td>
<td>100</td>
<td>CL 1</td>
<td>12.7-437</td>
<td>5.71±0.5</td>
<td>2.49±0.3</td>
</tr>
<tr>
<td>Diethylhexyl phthalate (DEHP)</td>
<td>91.3</td>
<td>CL 1</td>
<td>0.8-448</td>
<td>1.62±0.4</td>
<td>8.10±0.4</td>
</tr>
<tr>
<td>Decyl nonyl phthalate</td>
<td>93.5</td>
<td>CL 3</td>
<td>2.5-645</td>
<td>9.77±0.7</td>
<td>4.89±0.3</td>
</tr>
<tr>
<td>Decyl undecyl phthalate</td>
<td>82.6</td>
<td>CL 3</td>
<td>1.7-478</td>
<td>3.65±0.5</td>
<td>1.82±0.3</td>
</tr>
<tr>
<td>Undecyl dodecyl phthalate</td>
<td>4.3</td>
<td>CL 3</td>
<td>6.4-31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Diundecyl phthalate</td>
<td>45.7</td>
<td>CL 3</td>
<td>0.5-122</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Diheptyl phthalate</td>
<td>89.2</td>
<td>CL 3</td>
<td>0.7-50</td>
<td>1.34±0.5</td>
<td>6.7±0.4</td>
</tr>
</tbody>
</table>

DISCUSSION AND CONCLUSIONS

- 55 compounds from various classes were detected in dust
- Detected phthalates with uneven side chains show unstudied variability for the class of phthalates
- Concentration of novel phthalates in the same order as the concentration of well-known reference phthalates
- ΔCCSMM can function as an additional identification parameter by matching with established CCS-m/z trends
- Semi-quantification allows exposure assessment by giving an indication of concentration
- Exposure to phthalates through dust ingestion did result in no potential risk for toddlers, the most exposed group

Fig. 1: compounds detected in the dust with confidence level 1-3 and the subcategories they belong to. With PFR: phosphate flame retardant; PCP: personal care products.

Fig. 2: Comparison of ΔCCSMM values obtained for suspect phthalates with the CCS-m/z trendline established from ref. ΔCCSMM values of known phthalates and their metabolites (acetab). CL3 with uncertain alkyl chain branching.