

## A development history of PBDE reference standards and internal standards

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### Introduction

Polybrominated diphenyl ethers (PBDEs) are well-known flame-retardants that are used in a wide array of products. The health hazards and environmental concerns of these chemicals have attracted increasing scrutiny, PBDEs have been extensively monitored in all environmental matrices. On the basis of their persistence and remained reservoirs, the fate of PBDEs will need to be monitored for years to come.

Major PBDEs congeners have been developed as reference materials at Chiron since early 2000s. It has been challenging to develop higher brominated PBDE congeners (hepta-BDE, octa-BDE and nona-BDE) because of the difficulty of synthesis of pure isomers. New development on individual congener of hepta-BDE, octa-BDE and nona-BDE have been performed, new compounds have been synthesized successfully as pure reference materials.

Internal standards are needed for quantitative analysis of PBDEs. The benefit of using internal standards with physico-chemical properties similar to those of analytes is that both systematic and random errors will be minimized. Mono- and di-fluorinated PBDEs (F-PBDEs) have been developed at Chiron as internal standards, due to the closely similarity of F-PBDEs to the parent PBDEs. F-PBDEs as internal standards for GC-MS, GC-ECD, and GC-FID analysis have been investigated.

<sup>13</sup>C incorporated PBDEs (<sup>13</sup>C-PBDEs) have been used as internal standards for quantification of PBDEs. The preparation of <sup>13</sup>C-labelled products is inconvenient and laborious since the carbon skeleton have to be built up from small <sup>13</sup>C-labelled building blocks. A new project (EuroStars) started from 2016 has given us the possibility to develop <sup>13</sup>C-PBDEs as Internal standards. Primary study has been compare of F-PBDEs and <sup>13</sup>C-PBDEs synthesized on GC-MS and LC-MS analysis, to investigate the difference of chromatographic resolution relative to the parent PBDEs.

### Materials and methods

Beside the other native PBDEs developed earlier, the following native PBDEs have been synthesized recently as reference materials:

PBDE-184, 191 (hepta-BDE), PBDE-195, 197, 203 (octa-BDE), PBDE-206, 207 (nona-BDE).

The following F-PBDEs have been synthesized as internal standards:

3'-F-BDE-7, 3'-F-BDE-12, 4-F'-BDE-25, 4-F'-BDE-27, 2'-F-BDE-28, 6-F-BDE-47, 5,5'-diF-BDE-47, 6-F-BDE-66, 4'-F-BDE-69, 5,6-diF-BDE-85, 3-F-BDE-100, 3-F-BDE-119, 3,5-diF-BDE-119, 4'-F-BDE-160, 3'-F-BDE-183, 4',6-diF-BDE-201, 4'-F-BDE-208

The following <sup>13</sup>C-PBDEs are under development:

<sup>13</sup>C<sub>12</sub>-BDE-28, <sup>13</sup>C<sub>12</sub>-BDE-47, <sup>13</sup>C<sub>12</sub>-BDE-66, <sup>13</sup>C<sub>12</sub>-BDE-85, <sup>13</sup>C<sub>12</sub>-BDE-99, <sup>13</sup>C<sub>12</sub>-BDE-99, <sup>13</sup>C<sub>12</sub>-BDE-100, <sup>13</sup>C<sub>12</sub>-BDE-138, <sup>13</sup>C<sub>12</sub>-BDE-153, <sup>13</sup>C<sub>12</sub>-BDE-154

Evaluation of F-PBDEs and <sup>13</sup>C-PBDEs as internal standards for GC-MS and LC-MS analysis:

6-F-BDE-47, 5,5'-diF-BDE-47 and  $^{13}\text{C}_{12}$ -BDE-47 were added as internal standards into native BDE-47 solutions in different concentrations and analysed by GC-MS and LC-MS. Different retention time of the F-PBDEs were observed from the native analyte, while the  $^{13}\text{C}$ -PBDE internal standards co-eluted with the native compounds.

## Results and discussion

F-PBDEs are much easier to synthesize compared to  $^{13}\text{C}$ -PBDEs, and are therefore cost-effective:

The study on comparison of F-PBDEs and  $^{13}\text{C}$ -PBDEs as internal standards has shown that F-PBDEs eluted slightly differently than their native analytes, It is possible to design retention time for optimal elution rate by using ortho-, meta or para-F-PBDEs. While the  $^{13}\text{C}$ -PBDEs coeluted with the native analytes.

Mono- and di-fluorinated PBDEs are closely similar to the parent PBDEs in terms of physico-chemical properties, and are ideal internal standards for GC-ECD, GC-FID and GC-MS.

$^{13}\text{C}$ -PBDEs can not be used with GC-ECD since they are coelute with the native compounds.  $^{13}\text{C}$ -PBDEs are ideal internal standards for MS, especially GC-MSMS and LC-MSMS detection, since they can compensate for ion suppression effect than F-PBDE internal standards in biological samples.

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