

#### Mo-SY-B3.5

#### Using PCB signatures and enantiomer fractions for source identification and to age date exposure

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Polychlorinated biphenyls (PCBs) are a group of 209 chlorinated organic compounds that were widely used throughout the 20th century. While PCBs have been largely phased out of commercial/industrial use, they remain an important legacy contaminant and can still be found in closed systems in some countries as dielectric fluids in electrical equipment and transformers. Many transformers containing PCBs are in the process of being replaced which presents a potential for human exposure. In these instances it is important to not only determine the extent of any exposure and risks to human health, but to also establish the source and age date exposure.

To achieve this, detailed polychlorinated biphenyl (PCB) signatures comprised of over 80 congeners and chiral Enantiomer Fractions (EFs) of CB-95, CB-136 and CB-149 were measured for 30 workers at a transformer dismantling plant. Approximately 1.5 g of serum was extracted and PCB signatures were created through analysis by comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC-TOFMS), and EFs calculated following analysis by gas chromatography with high resolution mass spectrometry (GC-HRMS). A total of 84 PCBs were identified in the serum samples with concentrations of the 7 indicator PCBs ranging from 11-350 ng g<sup>-1</sup> of serum (1.2-39 µg g<sup>-1</sup> lipid). PCB signatures were interpreted using principal component analysis (PCA) which distinguished workers with background or recent exposure from those with prolonged occupational exposure. Occupationally exposed individuals had a similar PCB profile to Aroclor A1260. However, individuals with prolonged exposure had depleted proportions of several PCBs that are susceptible to metabolism (CB-95, CB-101 and CB-151) and elevated proportions of PCBs that are resistant to metabolism (CB-74, CB-153, CB-138 and CB-180). The results also identified a third group of workers who appeared to have been exposed to an additional source of PCBs. The results show near complete removal of the CB-95 E2 enantiomer in some samples, indicating that bioselective metabolism or preferential excretion of one enantiomer occurs in humans. By considering PCB concentrations along with detailed congener specific signatures it was possible to identify different exposure sources, and gain an insight into both the magnitude and duration of exposure.