Addressing the Challenge of Chloroparaffin Quantification in Environmental Samples: Development of Common Calibrant Solutions for SCCP Analysis.

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Introduction: Chlorinated paraffins (CPs) are complex mixtures of polychlorinated alkanes, with variable chain length and degree of chlorination. Commercially available CPs are often sub-divided according to their carbon chain length into short- (SCCPs, $C_{10\text{-}13}$), medium- (MCCPs, $C_{14\text{-}17}$) and long-chain CPs (LCCPs, $C_{>17}$), with each class comprising thousands of congeners. Once released into the environment, SCCPs are known to be ubiquitous, persistent, bioaccumulative and toxic environmental contaminants. However, despite analytical advances in recent decades, CP analysis in environmental and food samples remains extremely challenging. The scientific community has not yet established a satisfactory degree of comparability and accuracy between methodologies and laboratories carrying out the testing[1]. To reduce measurement uncertainty and develop, harmonise and implement validated methods of analysis for CPs, there is an urgent need for relevant, highly characterised CP reference materials. In 2019 we launched the Eurostars-funded project CHLOFFIN followed by the EU REVAMP and GreenREF projects to address this issue. One of the ultimate goals of these projects is to develop CP standards, with defined composition and response factors, which can be used to mimic industrial mixtures, and which can then be used for the certification of individual CPs in environmental and food reference materials. We describe the synthesis, characterisation and production of a synthetic mixture of well-defined CP single isomers as a reference material, known as a SCCP common calibrant, as well as the production of a complex mixtures of SCCPs with defined purity, carbon chain lengths (C_{10}-C_{13}) and chlorination ($Cl_{2\text{-}10}$), both of which have been incorporated into a round-robin testing programme and reference material certification programme coordinated by the European Union Joint Research Centre (JRC).

Materials and Methods: Individual SCCPs were prepared by chemical synthesis methods designed to produce individual CPs with defined chlorine positions and numbers. Five single congeners were selected for use in a SCCP common calibrant solution, produced either in isooctane or acetonitrile, in a metrologically traceable manner. The identity and chromatographic purity of each congener was confirmed/determined using GC-FID/MS and identity was confirmed by ^{1}H- and ^{13}C-NMR and net purity has been determined by quantitative NMR (qNMR) and or thermogravimetric analysis (TGA). For the SCCP mixtures, GC-EI-MS was used to estimate the proportions of different chlorination patterns in the mixture and GC-FID was used to determine the overall purity of the mixtures. Various NMR techniques were developed for chlorine content determination and for the SCCP single congeners are compared with theoretical values for single components and were used to determine the chlorine content of the single chain mixtures.

Results and Discussion: We have produced around 40 individual different chain-length CPs, more than 20 single-chain mixtures and technical mixtures. Five single congeners were selected for inclusion in a common calibrant solution produced in both isooctance and acetonitrile at concentrations ranging from 4-35 µg mL^{-1} and all had chromatographic purity >94%. The highly characterised SCCP single chain mixtures had a chromatographic purity >99%. The common calibrant has now been tested as part of a round-robin laboratory excercise conducted by JRC, and Chiron AS is now producing CP CRMs which are undergoing stability and homogeneity assessments**.**

Conclusions: We have prepared and characterised a range of SCCP single congener and SCCP single chain mixtures (known carbon chain length with a variety of degrees of chlorination) reference materials to support reliable CP quantitation in environmental and food samples, including the production of certified reference materials. The production and characterisation of these materials continues and is expanding to include MCCPs, LCCPs and ^{13}C-labelled analogues.

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References

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