Development of ^{13}C-labelled reference standards for the analysis of chlorinated paraffins

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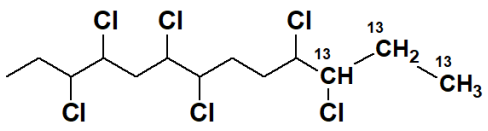
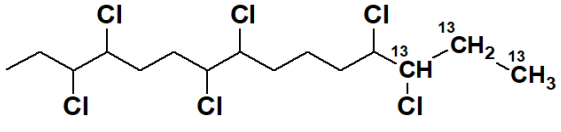
Introduction: The industrial chemicals of Chlorinated paraffins (CPs) need to be continuously monitored, the validation of analytical methods for the identification and quantification of CPs in various matrices is being hindered due to a lack of certified reference materials (CRM). These materials are required for the harmonization of analytical methods and the generation of comparable and reliable data. But there are not much suitable and generally accepted reference standards are available yet. As a result, errors in measurements within individual laboratories can occur. CP individual reference standards were developed at Chiron in the early 2000s, some of them are recommended as internal standards in the ISO 12010 method for water quality determination. In 2019 we launched the Eurostars project entitled CHLOFFIN and later the EU REVAMP and GreenREF projects. One of the ultimate goals of these projects are to develop standards with defined composition and response factors, which can be used to mimic the industrial mixtures and to be used for the certification of individual CPs in environmental and food samples and to certify the SCCP content in a fish CRM offered by JRC. Another ultimate goal is to develop ^{13}C-labelled CPs as intenal standards. These so-called new generation standards are useful in the quantification of CPs as well as helping in distinguishing the various congener groups according to carbon chain legnth and chlorine content.

Materials and Methods: Individual SCCPs, MCCPs and LCCPs were prepared by chemical synthesis. The synthesis routes were designed for the individual CPs with defined chlorines position and number. The optimized synthesis methods were applied for the synthesis of ^{13}C-labelled CPs. The chemical purity is analysed by one or several of the following GC-methods: GC-FID/MS, GC-MS-MS, high resolution GC-MS and GC-GC. Various NMR techniques are developed for chlorine content determination and are compared with theoretical values for single components. Further the NMR techniques are used to determine the chlorine content of single chain mixtures and technical mixtures.

Results: We have produced around 40 individual diffrent chain-length CPs, 8 ^{13}C-labelled individual CPs, and more than 20 single-chain mixtures. Two examples of ^{13}C-labelled SCCPs and MCCPs synthesized are as shown in **Table 1**. CRMs are produced by a combination of purity determination by GC-FID, identity by NMR and excess water, solvent and ash by TGA or qNMR in addition to stability and homogeneity assessment.

Table 1. Two examples of synthesized 13C-labelled CPs ($^{13}C_3$-$C_{13}Cl_6$ and $^{13}C_3$-$C_{15}Cl_6$)

	
3,4,6,7,10,11-Hexachlorotridecane-$^{13}C_3$	3,4,7,8,12,13-Hexachloropentadecane-$^{13}C_3$

Conclusions: Both individual native CPs, and ^{13}C-labelled CPs are prepared as reference materials and internal standards for the analysis of CPs. Single-chain CP mixtures have been synthesized for both SCCPs, MCCPs and some LCCPs as well. These reference standards will give more accurate measurements and are more suitable reference materials compared to the technical mixtures which are used as reference materials today.

Acknowledgements:
We thank Eureka-Eurostars programme, the EU Framework Programmes H2020-MSCA-ITN-2020 and H2020-INNOSUP, and the Norwegian research council for the fundings.

References:

1. Chiron AS, **13C-labelled Chlorinated paraffins and their preparation**, *Patent EP22162109.7* submitted 15.03.2022