##### ABSTRACT SUBMISSION FORM

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[x] Chlorinated paraffins

[ ] Remediation/destruction technologies

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**New generation of reference standards for chlorinated paraffins**

**– The Eurostars CHLOFFIN, the EU GreenREF and REVAMP projects**

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**Introduction:**

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. But these first-generation standards from Chiron have a chlorine pattern that is different than those found in technical mixtures and the environment.

In 2019 we launched the Eurostars project entitled CHLOFFIN and later the REVAMP and the 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. These so-called “new generation standards”, by comparation with the CPs standards synthesized at Chiron in early 2000’s, are useful in the quantification of CPs as well as helping in distinguishing the various congener groups according to carbon chain length and chlorine content.

**Materials and Methods:**

Individual single SCCPs, MCCPs and LCCPs were prepared by chemical synthesis. By designing the synthesis routes, individual CPs with defined chlorines position and number can be synthesized, examples of SCCPs synthesized are as shown **Table 1**. Further 13C labelled internal standard for SCCPs have been synthesized.

**Table 1. Examples of synthesized individual SCCPs standards, three generations:**

|  |
| --- |
| **Generation**  |
| 1659.10 | 1,1,1,3,9,10-Hexachlorodecane |  |
| 1650.11 | 1,1,1,3,10,11-Hexachloroundecane |  |
| 1652.12 | 1,1,1,3,11,12-Hexachlorododecane |  |
| 1654.13 | 1,1,1,3,12,13-Hexachlorotridecane |  |
| **Generation** |
| CLF12284.10 | 1,2,5,6,8,9,10-Hexachlorodecane |   |
| CLF14069.11 | 1,2,4,5,8,9-Hexachloroundecane |  |
| CLF14072.12 | 1,2,5,6,9,10-Hexachlorododecane |  |
| CLF14131.13 | 1,2,6,7,10,11-Hexachlorotridecane |  |
| **Generation** |
| 12286.10 | 2,3,5,6,8,9-Hexachlorodecane |  |
| New | 2,3,5,6,8,9-Hexachloroundecane |  |
| 15009.12 | 2,3,5,6,9,10-Hexachlorododecane |  |
| CLF14496.13 | 2,3,6,7,10,11-Hexachlorotridecane |  |

Single chain CP mixtures have been made by chlorination catalyzed by UV light. Single individual compounds have been analyzed for chlorine content using various NMR techniques and the results are compared with the theoretical values. A titration method for the determination of chlorine content was accredited. Individual compounds and the single chain mixtures were analyzed by GC-MS-MS, high resolution GC-MS and by GC-GC. Water, solvent and ash content was determined by TGA. Synthesized SCCPs single chain mixtures as examples are shown in **Table 2**.

**Table 2. Synthetized single chain SCCPs mixtures:**

|  |  |  |  |
| --- | --- | --- | --- |
| CLF14575.10-100-IO | Chloroparaffin single chain mixture **C10** Cl2-Cl6; 52.5% Cl (NMR) | CLF14803.10-100-IO | Chloroparaffin single chain mixture **C10** Cl4-Cl8; 58.4% Cl (NMR) |
| CLF14576.11-100-IO | Chloroparaffin single chain mixture **C11** Cl4-Cl7 52.3% Cl (NMR) | CLF14808.11-100-IO | Chloroparaffin single chain mixture **C11** Cl4-Cl8 57.6% Cl (NMR) |
| CLF15318.12-100-IO | Chloroparaffin single chain mixture **C12** Cl2-Cl7; 53.8% Cl (NMR) | CLF14809.12-100-IO | Chloroparaffin single chain mixture **C12** Cl4-Cl8; 57.3% Cl (NMR) |
| CLF14577.13-100-IO | Chloroparaffin single chain mixture **C13** Cl2-Cl7; 45.9% Cl (NMR) | CLF14687.13-100-IO | Chloroparaffin single chain mixture **C13** Cl5-Cl8(Cl9); 60.0% Cl (NMR) |

**Results and Discussion:**

We have produced around 40 individual single chain CPs, 13C-labelled individual CPs, and 10 single chain congener mixtures. Further single component mixtures are prepared for quantification together with defined mixtures and single chain mixtures.

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, and the results are compared with an accredited titration method and by elemental analysis. The results are consistent and the methods seems to be universal for CPs

CRMs are produced by a combination of purity determination by GC-FID, identity by NMR and excess water, solvent and ash by TGA in addition to stability and homogeneity assessment.

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