Mission sccpossible: A perspective view on the certification of the first reference material for short-chain chlorinated paraffins

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Introduction

Short-chain chlorinated paraffins (SCCPs) are industrial chemicals produced as technical mixtures of thousands of polychlorinated *n*-alkane isomers, defined by the carbon chain length C10-C13 and a chlorine content of 30 % to 70 % by mass weight. SCCPs are the object of regulations worldwide [1,2]. They are listed as priority substances of the EU Water Framework Directive [3a,b] and, as of 2017, have been added to the list of Persistent Organic Pollutants of the Stockholm Convention [4]. Despite their environmental relevance, the complexity of their analysis prevented so far an undisputed accurate quantification and the aspect of quality assurance/ quality control (QA/QC) still needs the most urgent attention [5]. The few interlaboratory comparisons reported in the literature show results which can vary up to 200 % [6-8]. Together with the participation in proficiency testing schemes, Certified Reference Materials (CRMs) are fundamental tools for external QA and are pivotal in assessing accuracy and ensuring comparability of measurement results in space and in time. This contribution presents the first steps in the planning of a possible certification of a RM for SCCPs, highlighting issues and envisaged difficulties while proposing a viable realisation of the project.

Materials and methods

In the view of assessing the feasibility of a certification project for SCCPs, the following soil, sediment and biota (C)RMs (already commercially available for other parameters) were screened with the support of the Vrije Universiteit Amsterdam, Environment & Health: BCR-481 (industrial soil), BCR-536 (freshwater harbour sediment), CCQM-K102 (freshwater sediment), ERM-CE100 (fish tissue), SRM 1947 (Lake Michigan fish tissue). The screening of two other CRMs is in progress, namely BCR-529 (industrial sandy soil) and BCR-530 (industrial clay soil). The four analytical methodologies applied for the screening are: carbon skeleton gas chromatography - low resolution mass spectrometry (CSk-GC-LRMS), GC electron capture negative ionisation LRMS (GC-ECNI-LRMS), chlorine-enhanced atmospheric pressure chemical ionisation triple quadrupole time-of-flight high resolution MS (Cl^--APCI-QToF-HRMS) and two-dimensional GC micro-electron capture detection (GCxGC-μECD).

Results and discussion

In the analysis of SCCPs, the agreement of results obtained with analytical techniques based on different principles can be a real issue [9], mostly depending on the chlorination degree of the sample and on the poor

match of sample and calibration standard. In addition, the presence of medium- and long-chain chlorinated paraffins (MCCPs and LCCPs) and/or other halogenated compounds can create an important interference problem, especially when LRMS is applied [10]. The non-sensitivity of the ECNI detection mode for the lower chlorinated CPs (with less than five chlorine atoms) is a known reported drawback of this approach, which is also "blind" to higher chlorinated SCCPs with more than 11 chlorine atoms [9,11]. CSk-GC-LRMS and GCxGC-μECD are more universal methods for detecting SCCPs, but they are also not devoid of downsides. The CSk method suffers of potential overestimation due to degradation of longer chain alkanes (in this method the CPs are quantified via the respective alkanes) [12]. The application of the GCxGC brings notable improvement in the chromatographic separation, but it cannot be regarded as a routinely applicable method, given the non-trivial data analysis [13,14].

Screening results

Among the criteria guiding the choice of a suitable candidate reference material for SCCPs certification we focused on the following: 1) availability of a sufficient number of units to perform the different studies needed (homogeneity, stability and characterisation), 2) absence/reduced presence of interfering substances known to create problems in the SCCPs quantification, 3) representative levels of SCCPs, *i.e.* environmentally relevant and above the limit of quantification of the applied analytical methods, 4) sufficiently good agreement among the different analytical techniques applied.

Table 1 gives an overview of the screening results, with regard to the criteria set for selecting the best candidate RM. A more detailed publication comparing the results and evaluating the performance of the four different analytical techniques is in preparation. For the purpose of the certification, the availability of BCR-481 is questionable (low number of units), while both ERM-CE100 and CCQM-K102 (replaceable by the "twin" CRM ERM-CC537a) seem to be a good second choice, showing a possible inter-method RSD of ≈25 %, when the analytical technique showing outlying results is left out for technical reasons.

Table 1: Set criteria for selecting a candidate RM for SCCPs certification

(C)RM	Availability	SCCPs level [1]	RSD % among techniques [2]	Suitability	Remarks
BCR-481	questionable	high	72 (21)	yes	--
BCR-536	yes	appropriate	130 (n.c.)	no	limited agreement
CCQM-K102	yes (as ERM-CC537a)	appropriate	66 (27)	yes	high Cl content (69 %): possible problem for the ECNI-LRMS
ERM-CE100	yes	appropriate	150 (21)	yes	testing without freeze-drying in progress; high MCCPs levels
SRM 1947	n.a.	low	195 (n.c.)	no	high MCCPs levels; limited agreement
BCR-529	yes	not yet known	not yet known	?	testing in progress
BCR-530	yes	not yet known	not yet known	?	testing in progress

1) with regard to environmental relevance i.e. ng/g; 2) in brackets the RSD calculated excluding one technique giving outlying results, because of technical reasons.

n.a.: not applicable; n.c.: not calculated (more than one technique to be excluded)

Planning of the certification study

The process of certification of a RM requires the application of reliable analytical methods, which have been validated following commonly accepted internationals standards or guidelines [15,16]. Homogeneity and stability of RMs are key requirements that need analytical methodologies characterised by sufficiently low repeatability, while the accuracy of the methods is a must for the assignment of the certified property values. At JRC-Geel, not less than ten measurement datasets, ideally based on different sample preparation and clean-up as well as detection/quantification principles, are generally required for starting a chracterisation study.

It is thus easily understood why, so far, there was no attempt, to our knowledge, to start the certification of a RM for this class of halogenated compounds.

A recent paper of van Mourik et al. [8] reports an overview of four QUASIMEME interlaboratory studies conducted on SCCPs, providing good background data for identifying qualified laboratories for participation to a certification exercise. In addition, validation parameters of the methods employed can be retrieved from these intercomparison data, useful in evaluating the methods' performance.

Based on the results acquired during the screening, both the Cl^--APCI-QToF-HRMS and GC-ECNI-LRMS seem to be suitable candidate analytical techniques for the homogeneity and stability studies, with repeatability of 15-25 %.

As regarding the RM matrix, both fish and sediment are environmentally relevant matrices. On the basis of the coefficient of variation (CV) among laboratories in the QUASIMEME interlaboratory rounds, fish seems to be somehow more difficult to analyse, perhaps due to the low level of SCCPs in the samples used.

The planning of a certification exercise requires also the identity definition of the target measurand, its level and projected uncertainty of the certified value. In the case of SCCPs, limit values in the legislation are commonly referred as "total SCCPs" or "sum of SCCPs", without distinction among congener groups, carbon chain length or number of chlorine atoms.

The identity definition of the SCCPs raises already an issue with regard to the traceability of the value possibly assigned. The establishment of the metrological traceability of the certified value is a requirement to be addressed at the planning stage by the Reference Material producer [17]. In addition, SCCPs calibrants commercially available and commonly used by the laboratories are "not fully" characterised (with regard to purity) mixtures of SCCPs isomers. In some cases, technical mixtures (only characterised by the chlorination degree) are still used as calibrants, even though this has been demonstrated to significantly bias the quantification [18].

The synthesis of SCCPs as single isomer standards has gained momentum in recent years and many are currently available in the catalogue of several producers. In contrast to the technical mixtures containing often a undefined number of undefined isomers, the preparation of ad-hoc mixtures of synthesised and well-characterised single-compound SCCPs to be used as calibrant might be an improvement step. Nevertheless, it is not a guaranteed perfect solution because of the difficulty to match sufficiently well the chlorination degree and pattern of the SCCPs found in the samples. As mentioned above, in the case of the ECNI mode of detection, the response is highly dependent on the % Cl, small differences in chlorine content resulting in great difference in sensitivity, making the choice of a suitable standard crucial [19].

How could we possibly circumvent these problems in the lack of metrological traceability of SCCPs standards for the purpose of the certification study? One possible option could be to prescribe the use of a "common calibrant", sufficiently characterised for purity and properly matching the pattern of SCCPs in the sample, to all participating laboratories. The benefit of using a "common" standard in reducing the CV among datasets provided by different laboratories using different techniques has been shown, while not dramatically, in [8]. Most importantly, with respect to the certification study, the use of a "common calibrant", appropriately characterised and matching the

SCCPs profile in candidate CRM, in addition to bringing an improved accuracy in the measurement results, it would also provide the basis for a proper metrological traceability statement of the assigned values [20].

Conclusions and outlook

The QA/QC situation in the analysis of SCCPs is still far from being satisfactory. The three most important pillars for implementing a proper QA/QC system in analytical measurements are notable: interlaboratory comparisons, standard methods and (C)RMs. While recently the number of interlaboratory studies has remarkably increased and two ISO standard methods have been published for the analysis of SCCPs in environmental matrices [21a,b], the panorama of CRMs is still completely deserted. The JRC has started therefore looking into the feasibility of the certification of a Reference material for SCCPs, with the hope to provide soon the environmental laboratories with one important missing piece in the puzzle of the QA/QC establishment for the "*most challenging group of substance to analyse and quantify*" [22].

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