CURRENT STATUS OF ANALYTICAL METHODS FOR CHLORINATED PARAFFINS

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Introduction

Analysing chlorinated paraffins (CPs) is still extremely challenging. Both identification (i.e. separation and detection) and quantification aspects bring various difficulties for the analyst. Standardised methods for CP analysis are available from the International Standards Organization (ISO 12010:2012 for water, sediment, sewage sludge, suspended matter and ISO18635:2016 for leather). However, the recommended method based on gas chromatography (GC) coupled to electron capture negative ion (ECNI) low-resolution single-quadrupole mass spectrometry (LRMS) presents serious analytical challenges. Concentrations are usually reported on CP group level (i.e. the sum of short, medium and long-chain CPs - SCCPs, MCCPs, LCCPs), although last year the first steps have been made toward a congener group specific analysis for SCCPs by Yuan et al.[1] Congener-specific analysis is still not possible. This paper gives an overview of the recent trends in methods for CP analysis.

Materials and Methods

Identification

Since the late 1990s GC-ECNI-LRMS is the most commonly applied method for the analysis of CPs[2]. However, this method has many disadvantages, such as the incomplete separation by single-column GC, the low resolution as well as the low response of MCCPs and LCCPs and lower chlorinated CPs (CPs with less than 5 chlorine atoms).

Two-dimensional GC (GC×GC) could be a promising tool that we further explored. Korytar et al. were the first to apply this method for CPs[3]. We developed a different method based on GC×GC coupled to a micro-electron capture detector (GC×GC-μECD) and indeed it was able to detect and separate at least some of the lower chlorinated congeners (CPs with < Cl_5). However, separation between congeners still remained largely incomplete and LCCPs were hardly detected. When more individual CP standards will become available this method enables congener specific analysis, although it is, due to its high resolution, recommended to use high resolution time-of-flight MS (TOF-HRMS) instead of μECD.

The chlorine-enhanced atmospheric pressure chemical ionisation APCI-HR-ToFMS[4] is a very promising method due to the high resolution and fast acquisition time (< 4 min) as well as the ability to detect all CP groups including LCCPs. We adapted the chlorine enhanced method by increasing the resolution (21,500) and decreasing the declustering potential for higher sensitivity of the lower chlorinated CPs (CPs with Cl_{3-4}). This method achieves the required MS resolution needed for differentiation between congener groups as well as other compounds such as chlorinated olefins, can determine SCCPs, MCCPs and LCCPs, differentiates between them and has the potential for congener group specific analysis.

Quantification

Because of the chlorine-dependant response of CPs, the compositions (i.e. relative abundance of the congener groups) of these mixtures must resemble as much as possible those found in samples to prevent quantification errors. This is difficult in case of environmental matrices, particularly for biota, in which the composition might differ because of 'weathering' effects. The current available quantification standard mixtures cannot individually provide a quantification reference for the mixtures found in such samples.

Two promising methods are available to correct for this chlorine-dependant response, a deconvolution method[4], primarily used for data obtained by APCI-HR-ToFMS and the linear relationship between calculated chlorine content and response[2], previously applied on data obtained by GC-ECNI-LRMS, and recently applied by us for APCI-HR-ToFMS data. The first one has the potential for congener group-specific analysis for at least SCCPs[1]. It is important to achieve an R^2 >0.50 between the constructed pattern and the pattern found in the sample. The

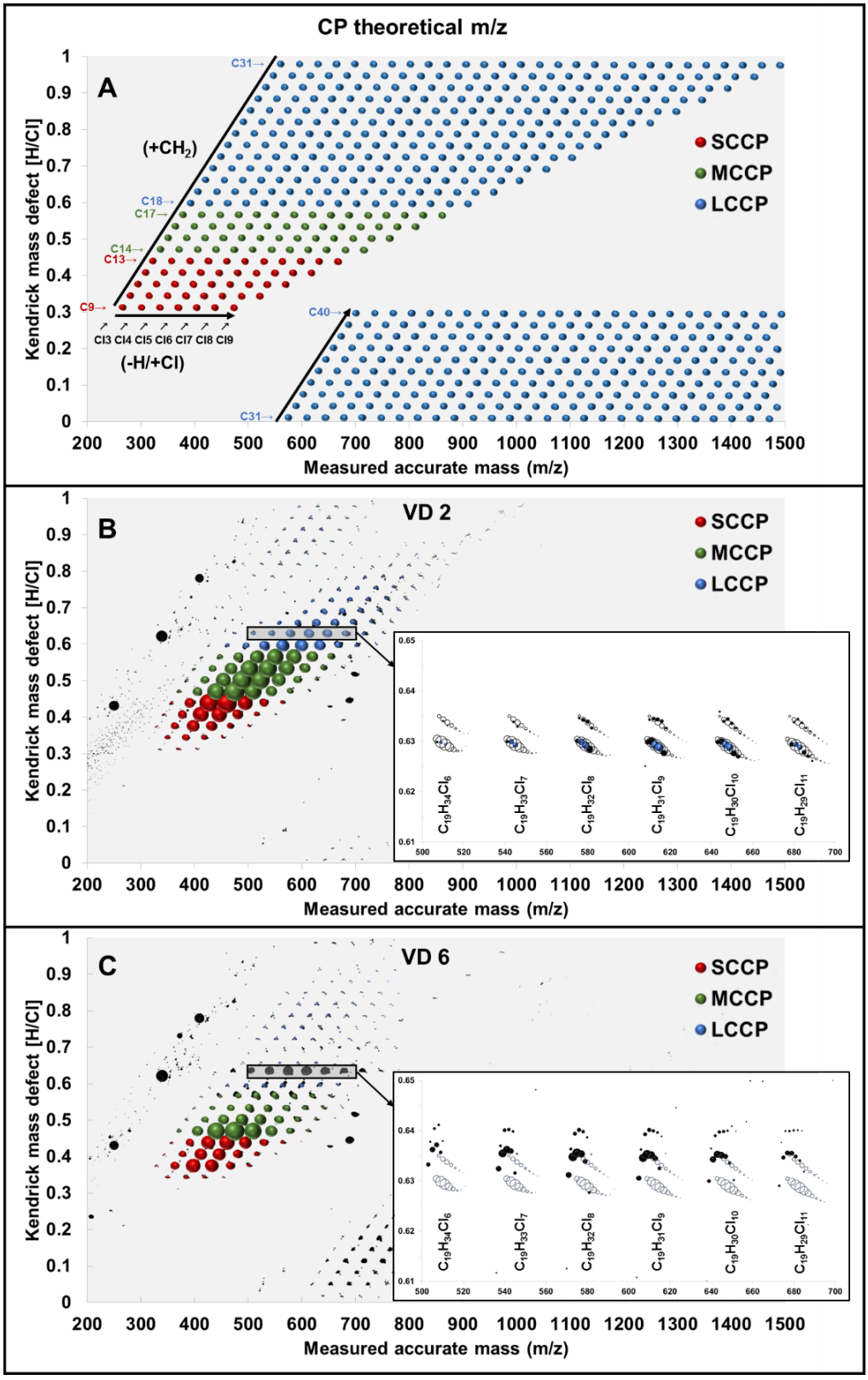

Figure 1. Non-traditional Kendrick MD plots, (A) constructed from the theoretical m/z quantitation and qualifier $[M+Cl]^-$ ions for CPs, (B and C) constructed for two dust samples from South Africa. The red spheres represent the quantifier and qualifier $[M+Cl]^-$ ions for SCCPs, the green for MCCPs and the blue for LCCPs the sphere size represents the instrument response. The enlarged region shows the theoretical m/z and ion intensity ratios for $C_{19}H_{34}Cl_6$ to $C_{19}H_{29}Cl_{11}$ depicted as black circles.

second one has the ability for carbon chain-specific analysis. The recently commercially available individual carbon chain lengths mixtures (i.e. C10 instead of C10-13, C14-17 or C18-20) with different chlorination degrees (LGC Ltd., United Kingdom) further facilitate this type of analysis. More mixtures with a composition pattern other than the current commercial standards (LGC) and more like those of Cereclor, Witachlor and Hüls are still needed.

Interpretation

For the interpretation of CP patterns Kendrick plots maybe helpful. We used non-traditional Kendrick plots to obtain information on the pattern of the CPs in dust samples from South Africa and to find evidence of possible interfering compounds (Figure 1). The non-traditional Kendrick MD plots were constructed by converting the measured IUPAC m/z to [−H/+Cl] mass scales corresponding to the mass of a chlorine atom minus the mass of a hydrogen atom.

Accurate H/Cl scaled mass=Accurate mass (IUPAC mass) ×(34/33.961028)
H/Cl scaled mass detect=nominal mass (rounded)- accurate H/(Cl scaled mass)

As shown in Figure 1, the Kendrick MD plots are graphically constructed as bubble plots by positioning the accurate masses on the x-axis and the corresponding H/Cl scaled mass defects on the y-axis with peak intensity as the bubble size. The CP congeners with the same carbon chain length (C_9 to C_{40}) and increased degree of substitution (> Cl_3) are positioned on horizontal lines separated by H/Cl substitution. The congeners with the same degree of substitution and increased carbon chain length are positioned on diagonal lines.

Results and Discussion

In general, reporting total SCCPs, MCCPs or LCCPs, let alone total CPs, is unlikely to be very meaningful from a fate, toxicological and hazard potential context. The uptake, and biological persistence and potential health effects of CPs are all likely structure-dependant. Different alternatives are congener-specific analysis, congener group-specific analysis (e.g. $C_{10}Cl_5$, $C_{10}Cl_6$), and analysis per carbon chain length and different chlorination degrees (e.g. C_{10} 50% Cl).

Given the current developments, it is now prudent to start focusing more on the analysis of congener groups, or at least carbon chain lengths with different chlorination degrees, rather than the groups (i.e. ΣSCCPs, ΣMCCP, ΣLCCPs) to better understand their hazard potential. Attempts are being made to make individual standards available, but will take some time. Also, attempts are being made to produce a certified reference material. Given the efforts currently being made by many laboratories, it may be expected that a mature analytical method will emerge in the coming years. Because of the limitations on the use of SCCPs, it may be expected that MCCPs will be the most important CP group to focus on.

References

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