Determination of Short-Chain Chlorinated Paraffins with the Carbon Skeleton method: investigation of the efficiency of the Pd catalyst liner

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Short-Chain Chlorinated Paraffins (SCCPs) are highly complex technical mixtures of polychlorinated *n*-alkanes with a carbon-chain length of C_{10}-C_{13} and chlorine content up to 70 %. Their production at EU level is banned, but their past widespread uses, together with the demonstrated persistence, raised concerns regarding their long-term environmental impact, especially for the aquatic system. For this reason, the European Union has included SCCPs in the list of the priority substances of the Water Framework Directive. The recent Directive 2013/39/EU (EUROPEAN COMMISSION 2013) confirms values of Environmental Quality Standards (EQSs) for this class of substances in surface and inland waters of 0.4 µg L^{-1} and 1.4 µg L^{-1} as annual average and maximum allowable concentration, respectively.

The quantification of SCCPs in environmental matrices is very challenging due to the complexity of their mixtures made up by thousand isomers. While a number of analytical methods were developed for their analysis in solid matrices like soil, sediment, dust and biota, for the determination of SCCPs in water the ISO 12010:2012 is the only standard method available (ISO 2012). This method is based on GC-ECNI/MS and can reach the established EQSs (GEIß 2012), but it entails the application of a multiple linear regression as calibration function and has limitations linked to the dependence of instrument response on the chlorination level and to the non-complete selectivity between SCCPs and Medium-Chain Chlorinated Paraffins.

On the basis of the outcomes of previous work carried out at JRC-IRMM, which lead to the validation of a method for the analysis of SCCPs in soil and sediments applying the Carbon Skeleton technique (PELLIZZATO 2009), the results of further investigation on the Pd catalyst performance are presented. The catalyst, used for the dechlorination/hydrogenation of the SCCPs to the corresponding *n*-alkanes (C_{10}-C_{13}), revealed to be a site for degradation of *n*-alkanes, to the detriment of the accuracy of the technique. The degradation of the *n*-alkanes, formed *in-situ* in the catalyst through hydrogenation of the SCCPs, is relevant at concentration values around the EQS level and is a key point for improvement of the Carbon Skeleton method.
Hence, alternative approaches to avoid the degradation were investigated: 1) the application of an *on-line* GC precolumn coated with a film of Pd catalyst, 2) the reduction in the quantity of catalyst used, 3) the activation of the catalyst with a reducing agent as suggested by Steinberg and Emerson (STEINBERG & EMERSON 2012). The results obtained in these experiments are presented. Unfortunately, degradation of *n*-alkanes to a different extent was observed all the time.

References:

- European Commission Directive 2013/39/EU of the European Parliament and of the Council of 23 October 2000, Off. J. Eur. Union L327, 1 (2013).
- F. Pellizzato, M. Ricci, A. Held and H. Emons Accred Qual Assur 14 (2009) 529-540.
- S. Geiß, M.Schneider, G. Donnevert, J.W. Einax, N. Lettmann, A. Rey, H. Lepper, B. Körner, T. Prey, B. Hilger, M. Engelke, M. Strub, H. Adrien, G. Sawal, D. Löffler, T. Schillings, I. Hussy, P. Steinbichl, S. Scharf, A. Ruderisch, J.E. Olmos, F.J. Santos and A. Bartolome, J. Caixach Accred Qual Assur 17 (2012) 15-25.
- ISO 12010:2012 Water quality - Determination of short-chain polychlorinated alkanes (SCCPs) in water – Method using gas chromatography-mass spectrometry (GC-MS) and electron capture negative-ion chemical ionization (ECNI).
- S.M. Steinberg and D.W. Emerson, Environ Monit Assess 184 (2012) 2119-2131.

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