Paper C18

Determination and quantification of Polychlorinated Alkanes in leather by gas chromatography and mass spectrometry

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Nowadays, consumer protection is an important concern in the leather industry and the number of controlled chemical substances included in different regulations is increasing. Short PolyChlorinated Alkanes (sPCAs) are a class of substances recently declared as potentially toxic. sPCAs were first regulated by the European directive 2002/45/CE that was later replaced by the appendix 17 of the REACh regulation.

An analytical protocol was developed to quantify sPCAs in leather. The ground leather sample is first extracted by hexane under ultrasound. Next a clean-up step gives an extract that can be analysed by a gas chromatograph coupled with a mass spectrometer in electron capture negative ionization mode (GC-ECNI-MS).

The leather sample was first ground in small particles and spiked with hexachloroundecane as the internal standard, then it was extracted with hexane in an ultrasonic bath for 1h at 40°C. Next the extract was evaporated to near 1 mL then filtered through a 10 mm i.d. chromatography column filled with 5g of 20 µm florisil. The filtrate was concentrated and re-dissolved in 5 mL of isooctane. The great number of compounds and isomers (several millions) making industrial PCAs make impossible to separate each of them individually. So the PCAs quantification is based on the integration of the global signal obtained for specifics ions at a particular GC retention time. The integrated signal is associated to multiple linear regression analyses.

The method was optimised and validated with a calibration sPCAs concentration between 0.15 mg/L to 1 mg/L with a sPCAs chlorine level between 51.5 % to 63 %. The internal standard concentration was set at 0.1 mg/L. The limit of quantification (LOQ) was validated at 0.4 mg/L that correspond to 2 mg/kg (2 ppm) in the leather sample with a significant uncertainty of at least 10 %.

The goal of our work is to design an usable quantitative analysis of sPCAs with a LOQ level widely under present regulation requirements and using an original approach for leather test. The multiple linear regressions with which the results are obtained were not dependent on the carbon number and chlorine content in the studied sample.

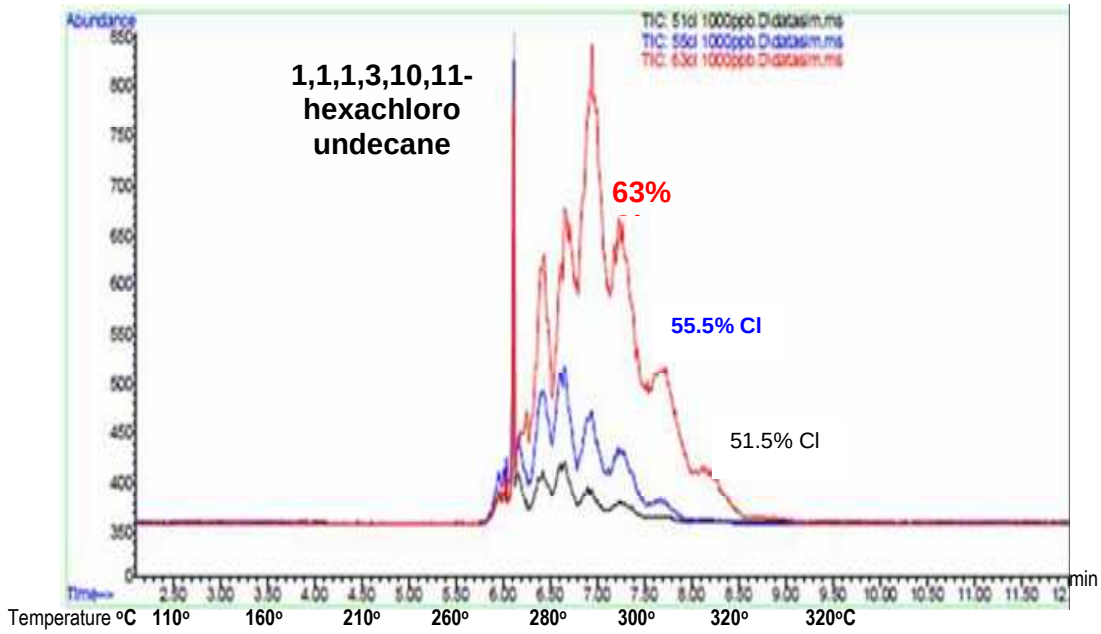

Figure 1: Overlay chromatograms of the same injected mass of short PCAs with 51.5%, 55.5% and 61% chlorine content (massif of peaks between 5.8 and 9.0 min) and hexachloro-undecane (fine peak at 6.10 min) in SIM mode (ion MS current for the sum of m/z 327, 375, 409, 423, 362 and 364). The abscissa has both a time (min) scale and the corresponding column GC temperature scale.

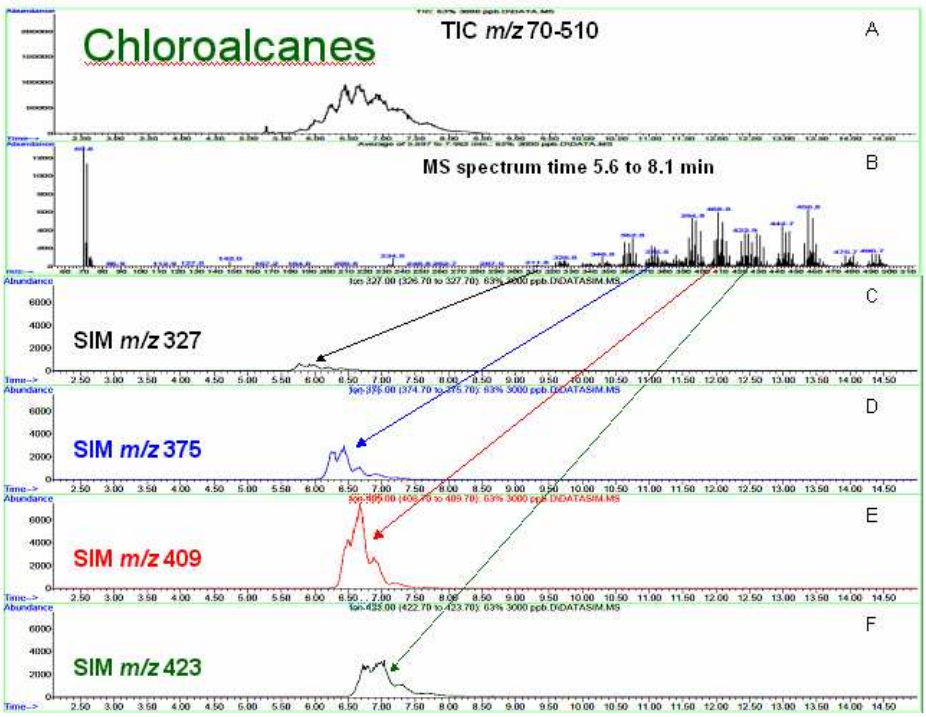

Figure 2: GC-ECNI-MS chromatograms with a DB-5ms capillary column (15 m, 0,250 mm i.d., 0,25 µm film thickness) of PCAs mixture with a chlorine content of 63% at 3 mg/L, (A) TIC, (C to F) SIM of specific ions choosed for quantitation (m/z 327, 375, 409 and 423). (B) mass spectrum of the entire PCAs retention time.

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