THE POTENTIAL OF SOFT IONIZATIONS FOR ANALYZING CHLORINATED PARAFFINS

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Introduction

Chlorinated paraffins (CPs) are mixtures of polychlorinated n-alkanes containing over thousands of congeners and isomers. Due to the complexity of the composition, CPs are one of the most challenging chemicals for the analytical scientists. In the instrumental point of view, gas chromatography (GC) is widely employed to separate organochlorines from CPs, especially short-chain and medium-chain CPs (SCCPs and MCCPs)[1]. Liquid chromatography (LC) is also applied to determine CPs, especially long-chain CPs (LCCPs)[1]. In order to separate SCCPs from MCCPs, two-dimensional GC (GC×GC) is a promising tool because of its superior separation power and peak capacity[2-3].

Electron capture detector (ECD), flame ionization detector (FID), and mass spectrometry (MS) are used as detectors in the CP analysis. MS is the most acceptable detector for CPs. Various ionization sources have been tested. They include electron ionization (EI), negative chemical ionization (NCI), electron capture negative ion (ECNI), Metastable atom bombardment (MAB) and positive chemical ionization (PCI) for GC-MS and GC×GC-MS, negative atmospheric pressure chemical ionization (APCI) and negative electro spray ionization (ESI) for LC-MS[1]. The standard EI with electron possessing 70 eV of kinetic energy is the most common ion source for GC-MS. However, it can only provide the information of total CPs. The information of individual congeners is hindered due to the nonspecific fragmentation pattern caused by high energy. NCI and ECNI are widely applied in the studies of CPs. The intensity of fragment ions [M-Cl]$^-$, which present the information of the precursor congeners, are highly enhanced by NCI and ECNI. However, the discrimination of lower chlorine number congeners (below 5) is the disadvantage of these ionization sources. In recent years, other soft ionizations such as cold EI, low energy EI, field ionization (FI) and photoionization (PI) showed their advantages in the isomeric identification of hydrocarbons.

In this study, state-of-the-art GC×GC-time of flight (TOF) MS coupled to soft ionizations PI and low energy EI was applied to analyze SCCPs. We aimed to explore the potential of the soft ionizations besides NCI or ECNI in the area of CPs.

Materials and methods

A SCCP standard mixture with chlorine content of 55% was used to exam the performance of different ion sources. Hexane was used as dilution solvent. The analyses were conducted on a GC (7890B, Agilent Technologies, Wilmington, DE, U.S.A.) equipped with Zoex thermal modulator (Zoex Corporation, Houston, U.S.A.). A TOFMS with a PI-EI combined ion source (JMS-T200GC "AccuTOF GCx-plus", JEOL Ltd., Tokyo, Japan) was coupled to GC×GC. The PI, 15 eV, 20 eV, and 25 eV EI were employed in this study. A normal column set (non-polar as 1st dimension, polar as 2nd dimension) was used. The instrument condition was described in our previous work[3]. Data acquisition was controlled on msAxel ver. 2.1 (JEOL Ltd.). The data were processed using GC Image ver. 2.5 (Zoex Corporation, Houston, U.S.A.).

Results and discussion

The different dilutions of SCCP standard mixture were measured under the same GC×GC condition with PI, standard (70 eV) EI, and low energy (15 eV, 20 eV, 25 eV) EI, respectively. The chromatograms obtained with PI, 70 eV EI and 15 eV EI were shown in Fig. 1. The chromatograms of 15 eV, 20 eV, and 25 eV EI did not show significant difference. Therefore, they are not presented in Fig. 1. As can be seen from the chromatograms, standard EI has the highest sensitivity, while PI has the lowest sensitivity. In general, the sensitivity of standard EI and low energy EI are acceptable for the SCCPs in the environment samples.

Besides the difference on sensitivity, the fragmentation pattern and the dominant fragment ions by PI and EI also show difference (Table 1). The dominant fragment ions in PI are [M-$C_5H_9Cl_3$]. While the predominant fragment ions in 15 eV EI are [M-$C_5H_9Cl_4$]. As seen from the mass spectrum of congener $C_{11}H_{17}Cl_7$ (Fig. 1), the quantifier fragment ions m/z 185 in 15 eV EI is much enhanced than in the standard EI. While, the nonspecific fragments such as m/z 41 and 55 are much weakened in 15 eV EI. The mass spectrum of PI is the tidiest with significantly improved intensity of quantifier fragment ion m/z 220. Moreover, the fragment pattern can assist us to understand the fragmentation pathway and further predict the isomeric structures.

Using the specific quantifiers of 24 congeners of SCCPs, the congener distribution is calculated. The congener patterns are constant among the low energy EI with different energies (Fig. 2). However, PI mode showed significantly different congener patterns compared with low energy EI. To be specific, PI overestimated the contribution of C_{10-11} - Cl_{5-7} congeners and underestimated C_{10-13} - Cl_{8-10} congeners. In general, PI had discrimination of longer carbon chains (C_{13}) and highly chlorinated congeners (Cl_{9-10}). This could be caused by the low sensitivity of PI. Since C_{13} and Cl_{9-10} congeners do not contribute much in SCCPs, their intensities are also much lower.
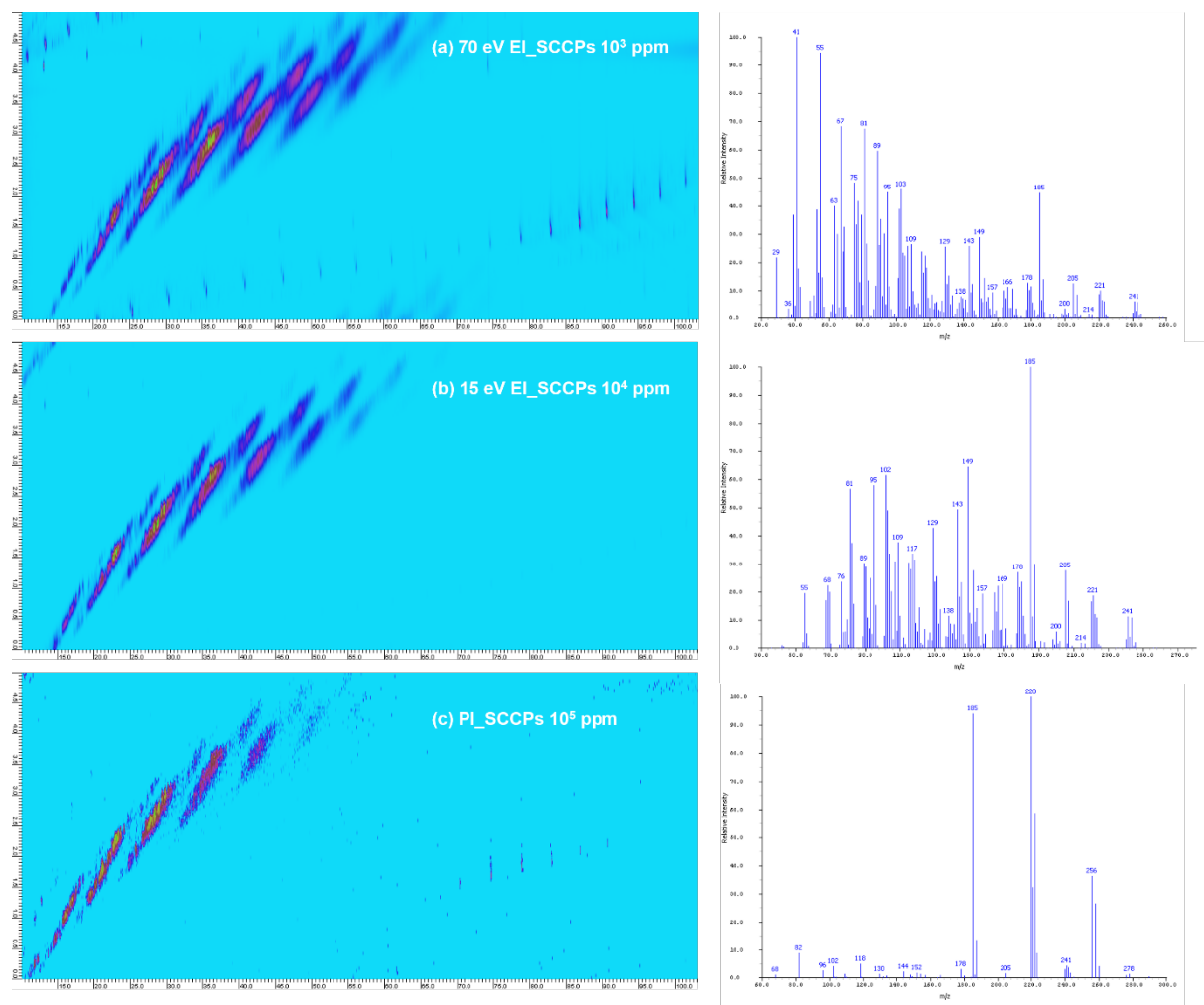
Figure 1. The chromatograms of SCCPs and the mass spectra of $C_{11}H_{17}Cl_7$ congener obtained with PI, standard EI, and low energy EI.

Table 1. The predominant fragment ions in PI and 15 eV EI.

PI	C10	C11	C12	C13
Cl5	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3]$
Cl6	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3]$
Cl7	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3]$
Cl8	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3]$
Cl9	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3] + 2$
Cl10	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3]$	$[M-C_5H_9Cl_3] + 2$	$[M-C_5H_9Cl_3]$

15 eV EI	C10	C11	C12	C13
Cl5	$[M-C_5H_9Cl_4] - 1$	$[M-C_5H_9Cl_4] - 1$	$[M-C_5H_9Cl_4] - 1$	$[M-C_5H_9Cl_4] + 4$
Cl6	$[M-C_5H_9Cl_4]$	$[M-C_5H_9Cl_4]$	$[M-C_5H_9Cl_4] - 1$	$[M-C_5H_9Cl_4] + 4$
Cl7	$[M-C_5H_9Cl_4]$	$[M-C_5H_9Cl_4]$	$[M-C_5H_9Cl_4]$	$[M-C_5H_9Cl_4] + 4$
Cl8	$[M-C_5H_9Cl_4]$	$[M-C_5H_9Cl_4]$	$[M-C_5H_9Cl_4]$	$[M-C_5H_9Cl_4]$
Cl9	$[M-C_5H_9Cl_4]$	$[M-C_5H_9Cl_4]$	$[M-C_5H_9Cl_4]$	$[M-C_5H_9Cl_4]$
Cl10	$[M-C_5H_9Cl_4] - 4$	$[M-C_5H_9Cl_4] + 2$	$[M-C_5H_9Cl_4] + 2$	$[M-C_5H_9Cl_4] + 2$
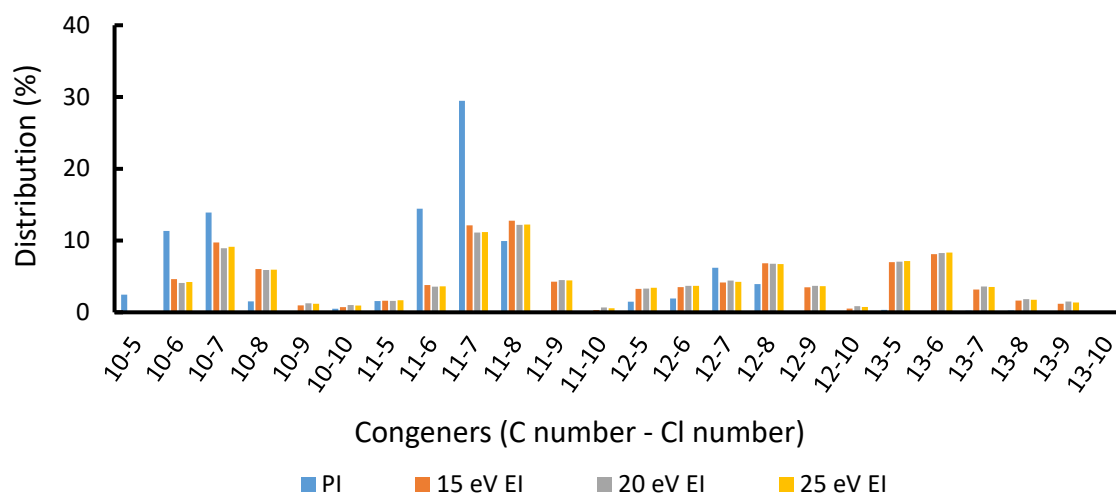
Figure 2. The congener distribution obtained with PI, standard EI, and low energy EI.

In summary, although the current technique of PI cannot reach to the same sensitivity level as EI and low energy EI, the tidy and informative mass spectrum reveal the potential and benefit that PI can bring to the analysis of CPs and possibly to the other organochlorines. Low energy EI, compared to standard EI, presented the enhanced intensity of the fragment ions which represent the precursor structure. To increase the sensitivity of soft ionization sources by the instrument vendors will benefit the analysis of CPs.

References
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