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IDENTIFICATION OF DECHLORANES BY GAS CHROMATOGRAPHY COUPLED TO TANDEM MASS SPECTROMETRY WITH ATMOSPHERIC PRESSURE CHEMICAL IONISATION (GC-APCI-MS/MS)

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1. Introduction

Flame retardants (FRs) are chemicals added to a wide range of consumer and industrial products in order to limit fire initiation and propagation in a context of fire safety. Some halogenated FRs have been registered to the United Nations Stockholm Convention annexes, due to persistence in the environment, long-range transport, bioaccumulation and toxicity. Although raising concerns, dechloranes constitute a group of polychlorinated FRs which are still used [1].

Dechlorane Plus (DP) in particular was produced for the first time by OxyChem in North America more than 40 years ago [2]. The technical product consists of the syn and anti isomers in a ratio of ~1:3. DP has a very high production volume (500-5000 $t.y^{-1}$) and is used worldwide [3].

In 2006, DP has been detected for the first time in various environmental matrices and in different aquatic and terrestrial biota, thus showing their bioaccumulation and biomagnifications potential [3]. Chen et al. [4], found that exposure to DP induces oxidative liver damage and leads to altered expression of genes involved in carbohydrate, lipids, nucleotides, and the energy metabolism in rats and mice. A need for data was therefore expressed regarding the occurrence of dechloranes along the food chain and their toxicity. As regard to analytical aspects, most of the authors use gas chromatography coupled to mass spectrometry (sometimes with tandem mass analysers) with electron impact (EI) or negative chemical ionisation (NCI) [5,6]. Such ionisation modes exhibit extensive (EI) or moderate (NCI) fragmentation, thus limiting specificity of monitored diagnostic ions. In the present work, we investigated the suitability of Atmospheric Pressure Chemical Ionization (APCI) as ionization technique for their identification in combination with MS/MS.

2. Materials and methods

2.1. Chemicals

Analytical standards of anti- and syn-Dechlorane Plus (Anti-DP, Syn-DP), Dechlorane 601, 602, 603, 604, 604CB and Chlordene Plus (CP) were obtained from Wellington Laboratories (Guelph, Ontario, Canada). $^{13}C_{10}$-labelled analytical standards of anti-DP, syn-DP and Dec-602 were purchased from Cambridge Isotope Laboratories (Andover, MA, USA).Working solutions were prepared at 1 $ng.\mu L^{-1}$ in toluene (Picograde®, LGC standards GmbH, Wesel, Germany) and stored at 4 ºC.

2.2. Instruments

A gas chromatography triple quadruple mass spectrometer (GC-QqQ) fitted with Electron Impact (EI) or Negative Chemical Ionisation (NCI) (Scion, Bruker) and a gas chromatography (7880 series, Agilent Technologies) triple quadruple mass spectrometer (GC-QqQ) fitted with Atmospheric Pressure Chemical Ionization (APCI), in protic (H_2O/MeOH 1:1, v/v) and dry conditions (Xevo, Waters) were used. In both cases, GC involved a ZB-5HT Inferno capillary column (15 m x 0.25 mm, 0.10 µm) (Phenomenex, Torrance, CA, USA). One µL was injected at 280 °C in the splitless mode. The oven temperature program started at 100 °C (held for 3 min) and rose to 325 °C at 15 $°C.min^{-1}$ (held for 5 min). Helium was used as carrier gas at 1 $mL.min^{-1}$. Auxiliary temperature was set at 320 °C (EI, NCI) or 380 °C (APCI). In EI mode, electron energy was set at 70 eV. In NCI mode, CH^4 was used as reactant gas. In APCI mode, make-up, auxiliary and cone gas flows were set at 400 $mL.min_{-1}$, 100 and 220 $L.h^{-1}$, respectively, using N_2 filtered through a moisture trap. A mixture of deionised water (>18 $mS.cm^{-1}$, BarnsteadNanopure® system, Thermo Scientific, Germany) and methanol (Picograde®) was placed in the source for protic conditions. Cone voltage was optimized to 30 V.

3.Results and discussion

3.1. Full scan

In accordance with literature [7], $[M]^{+\bullet}$ was not observed in EI (or negligible) while in-source fragmentation was extensive, leading to a fragment rather unspecific as base peak (e.g. $C_5Cl_6]^+$). More fragments were obtained by NCI, often corresponding to HCl losses, starting from [M-H] but leading to decreased sensitivity for a given ion. In APCI, we observed that $[M]^{+\bullet}$ was a major peak for all compounds, as illustrated in Figure 1 for anti-DP and DP-604, with quite similar mass spectra either in protic (H_2O/MeOH 1:1, v/v) or dry conditions. Dechlorane 602 also showed major $[M+H]^{+\bullet}$ ion, as well as $[M+MeOH]^+$ adduct in protic conditions. Other dominant ions were, for example, $[M-Cl]^+$ and $[C_5Cl_6]^+$. It was then relevant to select specific high mass ions for investigating collision induced fragmentation.

3.2. SRM method

Full scan mass spectra of selected precursor ions fragmented at 15 eV were recorded. Then, collision energy for 3 to 10 transitions per compound was optimised (0 to 40 eV, 5 eV step). The two most relevant ones in terms of sensitivity and specificity were finally selected for a highly specific Selected Reaction Monitoring (SRM) method (Table 1).

4.Conclusion and perspectives

The APCI ionisation was found quite soft for DPs, producing intense molecular ions relevant as precursor ions in MS/MS. As a perspective, after extraction/purification developments, this method will be evaluated and applied to food and Human samples in order to produce original occurrence data for the French population in a risk assessment context.

5. Ackowledgements

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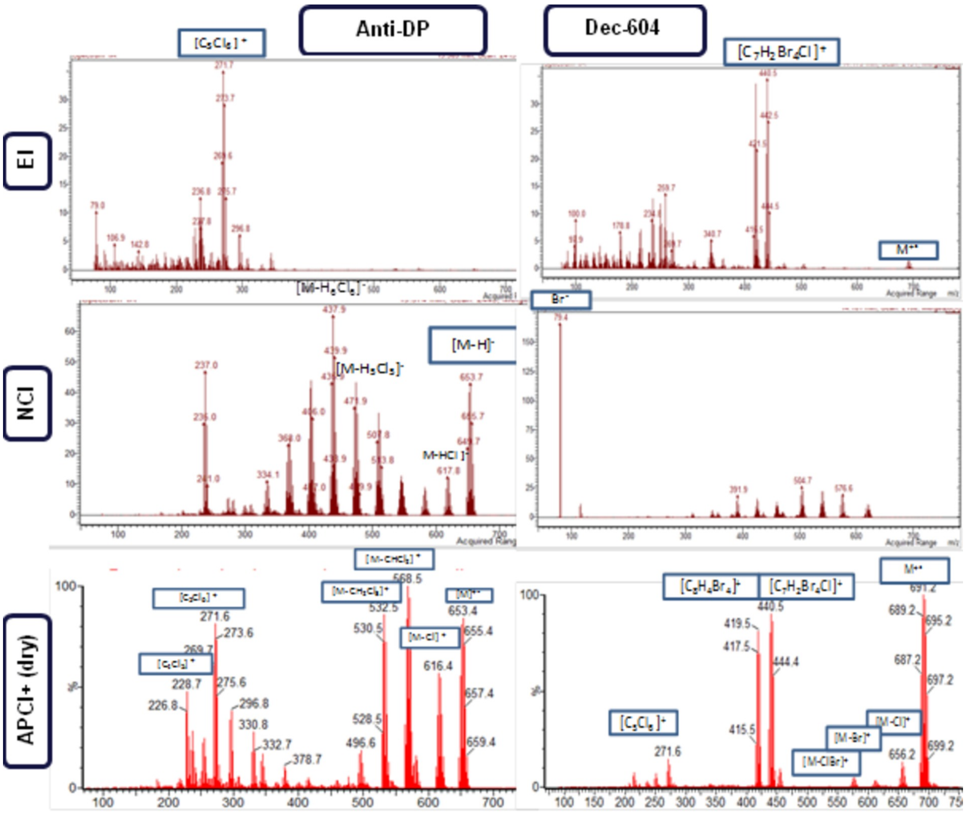

Figure 1: Obtained Full Scan mass spectra of anti-DP and Dec-604 in EI, NCI and APCI(+) (dry) modes.

Table 1: Optimised transitions for DPs by GC-APCI(+)-MS/MS.

Compound	Transition	Collision Energies (eV)	Retention time (min)
DP	653.7>228.9	25	14.80; 15.07
	568.8>228.9	25	
Dec-601	677.7>642.7	10	14.79
	638.7>330.9	20	
Dec-602	613.6>273.7	10	11.57
	613.6>514.7	15	
Dec-603	600.7>262.8	25	13.53
	637.7>602.7	10	
Dec-604	691.7>440.7	15	13.82
	419.7>259.9	25	

Compound	Transition	Collision Energies (eV)	Retention time (min)
Dec-604CB	613.6>362.7	20	12.25
	362.7>202.9	35	
CP	611.7>576.7	10	12.14
	611.7>271.8	10	
^{13}C-PCB-111	335.9>266	35	8.45
	337.9>268	35	
^{13}C-DP	577.8>232.9	25	14.80; 15.07
	663.7>232.9	30	
^{13}C-Dec602	623.6>278.6	10	11.57
	623.6>524.4	15	