

Atmospheric Pressure Gas Chromatography-Tandem mass spectrometry (APGC-MS/MS) for dioxins and PCBs analysis in food and feed

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Introduction

Two years ago we discussed in this journal the use of GC-MS/MS as a new potential option for confirmation of PCDD/Fs and DL-PCBs analysis in the framework of official food and feed control. Later, this new confirmatory approach has been extended to the auto-control of food and feed business operators. In this paper, we are taking stock of the different tools to perform dioxin analysis with mass spectrometers other than the so-called high-resolution MS sector instruments (HRMS), with a specific focus on Atmospheric Pressure Gas Chromatography-Tandem mass spectrometry (APGC-MS/MS). PCDD/Fs and PCBs analysis by GC-MS/MS is not a new concept, the first scientific papers relating the development of the method date from the nineties, mainly by using ion trap mass spectrometers. The method was able to easily detect trace levels of PCDD/Fs and PCBs in environmental samples. The lack of sensitivity to achieve sub-part-per-trillions (ppt) levels necessary for food and feed analysis made the technique inadequate and out of business for this particular analytical application. The new generation of bench-top triple-quadrupole MS recently launched on the market by several manufacturers has truly made a difference. The first studies and validations performed in food and feed highlighted the potentialities of the technique leading in 2012 to the amendment of the EU legislation by integrating the GC-MS/MS as confirmatory method (252/2012/EC)¹. At this stage, it is important to emphasize that only the last generation of triple quadrupole is able to meet the performance criteria of the EU legislation. Thus, it means that the risk succumbing to the temptation for 'non-dioxin' laboratories to start this very particular analysis, not equipped with the latest generation of triple quadrupole is high, with little chance to succeed. Indeed, the new EU Regulation amending 252/2012/EC (589/2014/EC)² is rather performance-based oriented, indicating that a confirmatory method can only be used if the method has demonstrated by a complete validation that all the quality and performance criteria listed in the above mentioned EU document have been met. Numerous analytical studies were performed within the European-National Reference laboratories (EU-RL/NRL) network to assess the capability of the GC-MS/MS method to be used as confirmatory method over the last two years. Depending on the GC-MS/MS used, most of these studies demonstrated the feasibility to achieve comparable analytical performances to GC-HRMS at low ppt levels.

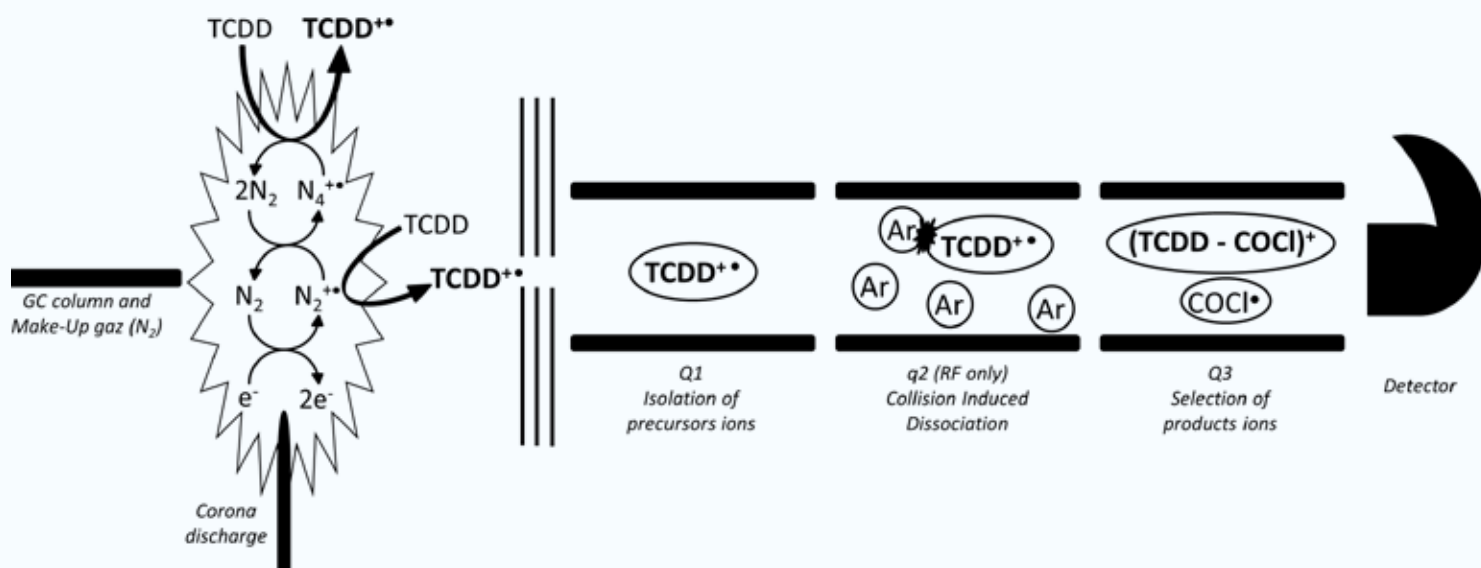
APGC-MS/MS

Among the different possibilities to analyze trace levels of dioxin and PCBs in food and feed, Atmospheric Pressure Chemical Ionization (APCI) is a soft chemical ionization technique that produces abundant molecular or pseudomolecular ions $[M^+]$ by charge transfer (Figure 1) or by protonation $[M+H]^+$. Although the first developments of APCI sources have been used to interface MS with liquid chromatography (LC), the ionization interface can also be connected to GC. The reduced fragmentation when using APCI makes the technique suitable for generating selective MS/MS fragments in the second quadrupole of the MS and sensitive Multiple Reaction Monitoring (MRM) transitions for numerous analytical targeted applications in MS/MS mode. This is in contrast to traditional Elec-



tron ionization (EI) at 70eV used in GC/MS, which generally suffers from extensive fragmentation and where the selection of the precursor ion is always a compromise between selectivity and sensitivity. In some cases, with less stable molecules, it might complicate the application of a quantitative MS/MS approach due to the lack of specific/abundant precursor ions. Recently, developments in APGC-MS/MS has resulted in very sensitive analytical applications for polycyclic aromatics hydrocarbons (PAHs)³, pesticides⁴, polybrominated diphenylethers (PBDEs)⁵ and PCDD/Fs and PCBs⁶. For instance, Kotz *et al.* showed that the absolute amount of 2,3,7,8-TCDD detected by APGC-MS/MS, by selecting two precursor ions, e.g. 320 and 322 m/z [M^+], giving the two product ions 257 and 259 m/z [$M-COCl$]⁺ (Figure 1), injected on GC column can go down below 10 femtograms (1fg = 10⁻¹⁵ g). It provides comparable sensitivity obtained with sector instruments (HRMS) based on standard calibration solution injected. For comparison with EI source GC-MS/MS, Kotz and co-workers have also reported of 50 fg absolute amount of 2,3,7,8-TCDD on column⁷. In an other study with a EI-GC-MS/MS, Fürst and co-workers achieved the same level of performances. The lowest calibration point for PCDD and PCDF congeners was 100 fg injected on-column with an excellent linearity from 0.1 to 10 pg injected on column⁸. L'Homme *et al.* reported an instrumental limit of quantification (iLOQ) of 0.016 pg/ μ L for 2,3,7,8-TCDD (80 fg on GC column) with also a EI-GC-MS/MS instrument⁹. All these works showed, on a limited number of samples, sufficient sensitivity for monitoring maximum and action levels for PCDD/Fs and PCBs in food and feed.

Figure 1: Analysis of 2,3,7,8-TCDD by APGC-MS/MS



A substantial gain using APCI compared to EI has been observed. The analytical performances, limited to instrumental injections, are most likely comparable because both PCDD/Fs and PCBs give rise to intense molecular ions by electron ionization. It is not the case for all the pollutants, it can be much better in favor of APCI as reported by Portolés and co-workers for pyrethroid insecticides⁴, where extensive fragmentation of those pesticides occurs in EI mode.

The sensitivity of the detection system is obviously pivotal for this type of analytical applications but femtograms of PCDD/Fs and PCBs injected from calibration solution are not real samples; measuring routinely at sub-ppt levels PCDD/Fs and PCBs is the true challenge and it requires the upmost sensitive detection system but the extraction and clean-up processes both play an important role. It definitely has influences on the quality and reliability of the analytical results. APGC-MS/MS or EI-GC-MS/MS techniques have demonstrated their potentialities on real samples at the levels of interest but long-term stability and performances in routine condition use still need to be assessed to completely assert that those instruments can be considered equal to magnetic sector instruments in terms of food and feed control under the EU legislation.

References:

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