GCXGC COUPLED TO FAST SCANNING QUADRUPOLE MS FOR TRACE ANALYSIS OF POPS

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As an alternative to the complex reference gas chromatography coupled to isotope dilution high resolution mass spectrometry (GC-IDHRMS) approach, new analytical methods are explored. Based on our previous investigations on the use of comprehensive two-dimensional GC coupled to time-of-flight MS (GCxGC-IDTOFMS) for the measurement of POPs, we currently evaluate the capabilities of GCxGC coupled to fast scanning low resolution quadrupole MS (qMS). The qMS can scan at up to 50Hz when operating in selected ion monitoring (SIM), offering the required sampling rate for narrow GCxGC peak characterisation. This instrument offers both electron impact (EI) and negative chemical ionization (NCI) to produce ions in the source. Advantages of NCI are known for a long time in terms of PCB analysis but it often suffers of lack or reproducibility and can make ID measurement difficult because of the limited availability of target ions. Both ionizations methods are investigated to evaluate the potential advantage of using GCxGC and NCI with this specific instrumental setup.

The stability of MS system was first investigated in regular GC to estimate the repeatability of measurements. A mass calibration tune was performed regularly and did show good response stability over time. All GCxGC parameters were optimizes to reproducibly produce adequate ^{2}D peaks. Three to four slices per peak were obtained for all analytes. The classical peak width in ^{2}D was 600ms. This resulted in a number of 10-15 scans across each slice and a good description of the peak shape for the scan rates that were used.

The spectral quality of this scanning instrument is good and allows proper quantification performances. Typical scanning MS mass skewing was observed across GC peaks but did not affect the quantification when based on averaged mass spectra. Both EI and NCI allowed isotope dilution quantification under good QA/QC criteria. For quantification, the two most intense ions for the natives and the two most intense ions for the label were followed. This permitted a maximum scan rate of 25 Hz in SIM. Calibration curves were established the same way we do for the ISO17025 GC-IDHRMS method. Ion ratios were checked and showed to be within a 20% range from theoretical ratios for both EI and NCI. QC charts testify for the good correlation between reference values and GCxGC values for PCBs and dioxins.

The same S/N ratio (S/N = 150 for the higher peak of the cluster for 1 pg injected) were obtained for SIM GCxGC-EI-qMS and for full-scan GCxGC-NCIqMS. A potential issue with NCI is however the low intensity of parent ion cluster for low chlorination level. This obviously makes ID quantification more delicate. A complete optimization of the ionization parameters (source temperature, reagent gas, gas pressure, …) is under consideration to optimize mass spectral quality and estimate if ID can still be performed in good conditions. The goal then is to perform SIM GCxGC-NCIqMS to attempt a validation study for quantification of PCBs and dioxins in biological samples.