

GCxGC-TOF-MS AND GC-MS-MS CHARACTERIZATIONS OF COMPLEX ENVIRONMENTAL SAMPLES CONTAINING DECHLORANE PLUS-RELATED COMPOUNDS AND CHLORINATED PAH

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Introduction

The application of comprehensive two-dimensional gas chromatographic separation (GCxGC) methods to the analysis of complex mixtures of volatile and semi-volatile compounds can provide dramatically improved separations compared to conventional one-dimensional GC methods. The increased peak capacity of GCxGC methods is further enhanced through the use of rapid mass spectrometric methods such as time-of-flight mass spectrometric (TOF-MS) detection^{1,2}. One-dimensional gas chromatographic analyses can be significantly enhanced through the application of tandem mass spectrometric (GC-MS-MS) approaches. While GC-MS-MS methods tend to be target compound methods, the use of common mass losses within a compound class provides the opportunity to develop compound class-directed GC analyses. We sought to compare the chromatographic outcomes of the application of comprehensive GCxGC-TOF-MS methods with GC-MS-MS methods on the same samples.

Dechlorane Plus (DP) is a heavily chlorinated, high production volume, flame retardant chemical that has been produced for over 40 years and has recently been found in air, water, sediments and biota worldwide³. In the course of the analysis of environmental samples containing DP and DP-related compounds, we found that there were a number of instances of peak overlaps in 1D-GC analyses using either 5%-phenyl or 50%-phenyl silicone chromatographic columns which may be improved through the application of GCxGC methods. Co-eluting substances included isomeric DP-related substances and dechlorinated DP compounds presumably arising from environmental degradation. We also wished to examine a rather extract from a soil sample collected at the site of a fire at a plastics recycling plant in Hamilton, Ontario in 1997. It is reported that about 400 tonnes each of poly(vinyl chloride) and polyurethanes were combusted during this 3-day fire. Preliminary analyses of this sample have shown that it is extraordinarily complex and likely contains thousands of semi-volatile species including high levels of dioxins and furans, chloro-bromo dioxins and furans, PAH and heavily chlorinated PAH.

Materials and methods

The Dechlorane Plus and related standards were purchased or provided by Wellington Laboratories (Guelph, ON); bottom sediment and sediment core samples were collected in the Great Lakes by the Ontario Ministry of the Environment and Environment Canada and prepared for analysis as described^{4,5}. A sample (~2g) of the Plastimet Fire soil sample was extracted with toluene using accelerated solvent extraction and the resulting extract cleaned up using a sequence of silica and alumina columns using a protocol published by the Ontario Ministry of the Environment⁶.

The GCxGC work was performed on an Agilent 7890 GC connected to a LECO Pegasus 4D GC-TOF-MS system (LECO Corporation, St. Joseph MI) outfitted with a 60 m 0.25 mm x 0.25 μ m film Rxi-5Sil MS column (Restek, Bellefonte, PA) as the first dimension and either a ~1 m 0.25 mm x 0.25 μ m film Rxi-17Sil MS (Restek) or a 0.10 mm x 0.10 μ m film BPX-50 column (SGE Analytical, Australia). The GC-MS-MS analyses were performed on a Varian 3800 gas chromatograph connected to a Varian 1200L triple quadrupole mass spectrometer equipped with a 30 m 0.25 mm x 0.15 μ m film DB-17ht column (J&W Scientific). The GC-MS-MS instrument was operated in the selected ion monitoring (SIM) mode, in the multiple reaction monitoring (MRM) mode and in the neutral loss scan mode. In the case of the neutral loss scan mode experiments, neutral

losses of 26 Da (loss of C₂H₂) and 60 Da (loss of C₂H³⁵Cl) were used to identify PAH and some chlorine-containing PAH.

Results and discussion:

The GCxGC-TOF-MS analyses of the Dechlorane Plus isomers and Dechlorane Plus-related compounds showed that peak overlaps that had been observed in previous 1D GC separations could be resolved using GCxGC methods. The chromatographic overlaps that had complicated previous 1D analyses of samples containing the 1,4-cyclooctadiene-DP isomers and vinylcyclohexene-DP isomers were resolved in two dimensions. This allowed for more facile and more comprehensive analyses of these minor components in sediment core samples obtained from the Niagara River Bar. This site lies at the mouth of the Niagara River, downstream of the Oxychem plant in Niagara Falls, New York; this plant is the sole known production site for DP in North America. Variations in DP-related compound compositions may provide insights into date of production of DP in a given environmental sample. The plant has been producing DP and DP-like compounds since the 1960's. The GCxGC method provides an unambiguous identification protocol for these isomeric species and can provide unique signatures of DP production for certain periods of time. The deconvoluting the pattern of dechlorinated DPs has also been a serious challenge for 1D GC methods. The GCxGC approach showed that the resolution of these dechlorination products could be improved dramatically.

The GCxGC-TOF-MS analysis of the Plastimet Fire extract showed that this sample contained a spectacular number of chemical substances. This sample not only contains high levels of dioxins and furans and PAH, there are many chlorinated PAH. Each PAH isomer is accompanied by a suite of chlorine-containing PAH isomers, typically with between 1 and 6 chlorines per PAH. As with methyl-substituted PAH there are a large number of possible isomers given the number of possible unique locations in some PAH. Isobaric PAH derivatives have similar to very similar chromatographic properties resulting in patterns wherein the homologous series of chlorine-containing PAH are nicely separated but the members of an isobaric group with a fixed number of chlorine atoms are very tightly clustered even with optimization of the separation using a long (60 m) first dimension column. We followed the recommendations of Blumberg et al.⁷ in the development and optimization of GCxGC methods to maximize the technique's peak capacity and resolution in the second dimension.

The GC-MS-MS analyses also provided useful insights into the composition of the mixtures by using first dimension columns of similar lengths and temperature programs. The neutral loss analyses allowed us to determine information about components within the clusters of components observed in the GCxGC experiments. Overall, the combination of GCxGC and GC-MS-MS analyses allowed us to deconvolute a large number of components in very complex samples.

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