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Extended Abstract (4 X A4 pages)

ION MOBILITY ENHANCED SEPARATION OF POLY-HALOGENATED DIOXINS AND FURANS IN CONTROLLED BURN SAMPLES

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Introduction

Chlorinated dioxins and furans are widely monitored persistent organic pollutants, which are produced from a range of sources. A much more complex, though equally important separation, the mixed chlorine and bromine dioxins and furans present additional complications to the analytical chemist. They represent a highly varied group of compounds with regards to both degree and position of chlorines and bromines, presenting an analytical challenge. For purposes of risk assessment, the ability to determine the array of these congeners present in samples is of particular interest. In order to enhance peak capacity to analyze these very complex mixtures, some studies utilize GCxGC[1]. Here we propose the use of ion mobility coupled with high-resolution mass spectrometry (IM-MS) in order to further characterize and isolate specific congener groups following GC separation. Complex burn site sample extracts containing these mixed groups of dioxins and furans were used to assess this approach, in which numerous proposed identifications were made in samples from simulated burns of electrical wire, circuit, foil and plastic.

Materials and methods

Atmospheric pressure ionization gas chromatography (APGC) utilizing a 60-M Rtx-5MS column was coupled to an ion mobility QTof MS system. Briefly, the GC oven temperature program started at 120°C and increased to 200°C at 35°C/min., then 280°C at 4.5°C/min. with an 8 min. hold, and a final ramp up to 330°C at 20°C/min. held for 15 minutes. APGC source conditions were optimized for charge transfer conditions, and a polysiloxane column bleed peak at 281.0517 was used for lockmass correction. Alternating full spectral acquisitions of elevated and low collision energy states were implemented in the MS method (HDMS[E]), in a collision cell following the IMS drift cell. Available standards of mixed bromo/chloro dioxins and furans were analyzed and used to determine retention times and accurate mass fragments. Samples from a simulated burn study representing typical accidental fire conditions were extracted using previously established methods for co-planar halogenated compounds prior to analysis on using the GC- QTof IM-MS system.

Results and discussion:

Work completed thus far indicates chromatographic separation of available standards using the single 60-M GC column. From these standards, accurate mass characteristic fragment ions could be determined, and their formulae either confirmed from existing data or deduced for the first time.). Additionally, drift times obtained from the passage of the ions through the N2 filled travelling wave drift cell were collected for each analyte. Those drift times were then calibrated to derive the collisional cross section (CCS) value of each ion, which is a unique parameter associated with the analyte. In addition to the measured mass of the parent and fragments and retention times of the known congeners, CCS values were used to make positive identifications in these samples. In order to assess the reproducibility of the CCS measurements, %RSDs across ten consecutive QC injections of the standards were calculated, as well as for retention times (Figure 1).
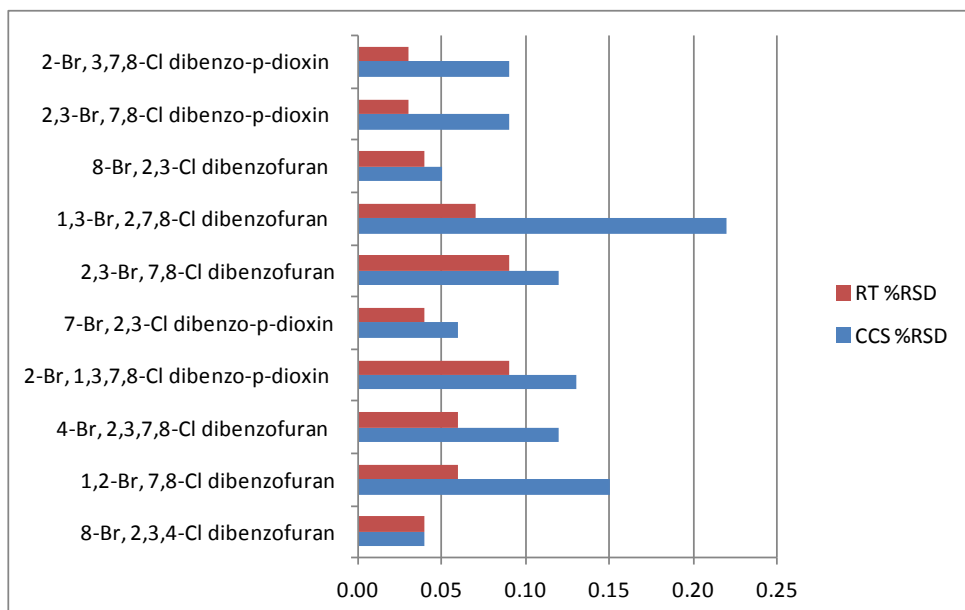
Figure 1: %RSDs for QC injections of mixed halogenated dioxins and furan standards indicate minimal variation across CCS measurements, and support the use of this parameter for use in identification purposes.

Sample analyses were performed on the burn study extracts indicating the presence of multiple congeners (Figure 2). Using isotopic distribution patterns and known fragments, the congeners not present in the solvent standard were confirmed (Figure 3). In addition, IM-MS also afforded the determination of CCS values for these compounds acting as a further identification and differentiation point. As standards are not available for most all of the various halogen substitutions theoretically possible, molecular formulae of these uncharacterized mixed halogenated dioxins and furans were used to mine the data, resulting in several observations across the samples. A combination of this information was used to indicate the proportion of specific mixed halogenated dioxins and furans (with respect to degrees and nature of halogenation) present within the various burn site samples. Lastly, as a strategy to deal with the very complex spectrum generated from these samples, post-acquisition spectral clean-up was possible by removing all spectral peaks from the display that do not share the same drift time as the selected analyte.
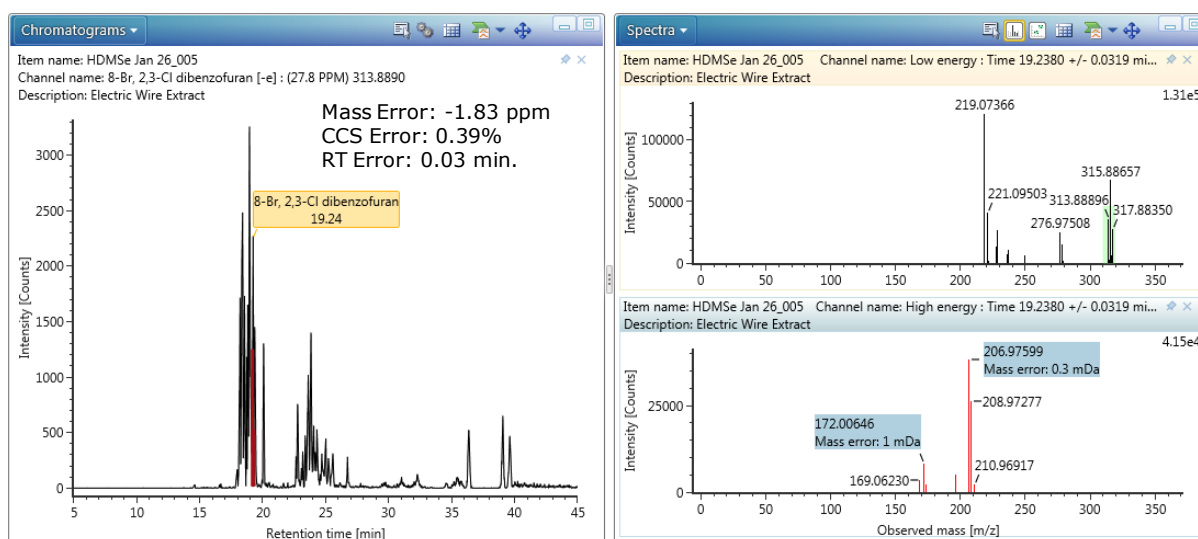
Figure 2: Identification of 8-Br, 2,3-Cl dibenzofuran in electrical wire burn sample extract, as confirmed by the presence of exact mass fragments established from the known standard, isotope distribution patterns, accurate mass measurement and conservation of CCS values and RT also from the known standard. The extracted ion chromatogram (EIC) indicates the presence multiple other congeners.
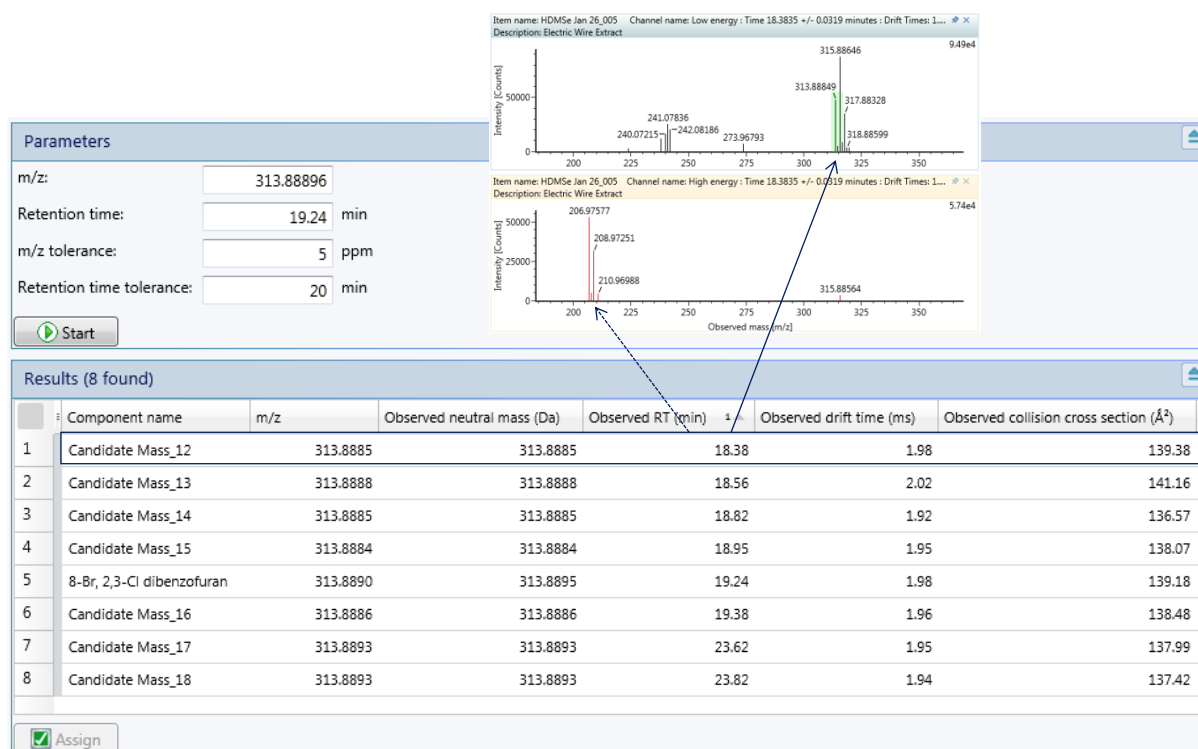

Figure 3: Further investigation of the other peaks associated with the EIC shown in Figure 2 indicated several other likely congeners. Software functionality allows for the searching of additional compounds that share the same mass as the identified component, based on different retention time and drift time separation. Their proposed identification was supported by the presence of the same fragment ions found for 8-Br, 2,3-Cl dibenzofuran. Observed CCS values were taken for the identifications and used to further characterize the ion mobility separations of these compounds. This approach was used for the various other mixed halogenated dioxin and furan identifications.

In addition to increasing peak capacity using ion mobility separation, differential separation of the various congeners (both between and across congener groups) is also being assessed. Additional constituents such as chlorinated polyaromatic hydrocarbons (PAHs), which have been described recently in industrial burn site fallout studies[2], are also being investigated in this work.

References: Use Times New Roman, pt 10

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