ANALYTICAL METHOD DEVELOPMENT FOR 2,4,6,8-TETRACHLORODIBENZOTHIOPHENE (TCDT) IN RIVER SEDIMENTS UTILIZING GCXGC-TOFMS AND APGC-TQS

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Introduction

A number of environmental studies have been performed to identify contaminants in the Passaic River in New Jersey. A particular contaminant of interest that emerged from these studies was 2,4,6,8-tetrachlorodibenzothiphene (2,4,6,8-TCDT). Not only has this compound been discovered in surface sediments in the river[1], but it has also been identified in marine organisms found in the river.[2] Other contaminants of interest discovered in both river sediment and the marine life include 2,3,7,8-tetrachlorodibenzo-p-dioxin and related polychlorinated dibenzo-p-dioxin and dibenzofuran (PCDD/F) species.

A potential source and pathway for creation 2,4,6,8-TCDT has been proposed.[3] One tool for source identification is by calculating the ratio of 2,4,6,8-TCDT to 2,3,7,8-TCDD recovered from the river sediment samples. Early studies on Passaic River sediment have struggled with misidentification of 2,4,6,8-TCDT as 1,2,8,9-TCDD due to the two compounds being isobaric (both have a nominal mass of 322) and require a mass resolving power in excess of 10,000.[3] Therefore, chromatographic resolution is crucial, as well as access to a reference standard for mass spectral comparison.

Materials and methods

Samples received were river sediment cores collected from the Passaic River in New Jersey. Sample preparation included an extraction step followed by sample clean-up. Samples were extracted in toluene using Soxhlet extractions. Prior to sample analysis, a two step sample extract clean up was performed, first using an acid/base silica column, followed by a reversible carbon/silica column. Prior to sample extraction, soil samples were spiked with a mix of ^{13}C labelled polychlorianated dibenzo-p-dioxins and dibenzofurans for isotope dilution quantification of both the dioxins and furans, as well as 2,4,6,8-TCDT.

Prior work in this area has reported difficulties with coelution of the chloro-thiophenes with the isobaric dioxins, and/or the addition of additional ions to be monitored, resulting in a decrease in overall sensitivity. Additionally, sample extract cleanup techniques have been potential sources of bias as 13C labels have not been commercially available for the chloro-thiophenes. Our work has demonstrated that assuming that they behave exactly as the dioxins and furans is likely in error.

Initial analytical work was performed using comprehensive two dimensional gas chromatography-time of flight mass spectrometry (GCxGC-TOFMS). This technique was utilized as both a sample pre-screening step, as well as to perform an initial quantification on samples before transitioning to a more sensitive mass spectrometer. The benefits of GCxGC-TOFMS include enhanced peak resolution as well as the ability to collect data over a large mass range.

Following GCxGC-TOFMS analysis, the samples were analyzed on an atmospheric pressure ionization gas chromatograph coupled to a triple quadrupole mass spectrometer (APGC-TQS). This instrument is beneficial for

its high sensitivity and highly selective MRM mode. Using this technique, a more accurate quantification can be performed, especially for dioxins and furans present at low levels.

Results and discussion

Using the electron impact (EI) source of the GCxGC-TOFMS, the mass spectra of 2,3,7,8-TCDD and 2,4,6,8-TCDT were collected. The fragmentation patterns were observed to be different between the two compounds, allowing for the two species to be distinguised from one another. The tetrachloro dioxins favor a mass loss of –COCl (-63 m/z) whereas the tetrachlorodibenzothiophenes favor the loss of a $–Cl_2$ fragment (-70 m/z). The comparison of the two characteristic spectra can be seen in Figure 1.

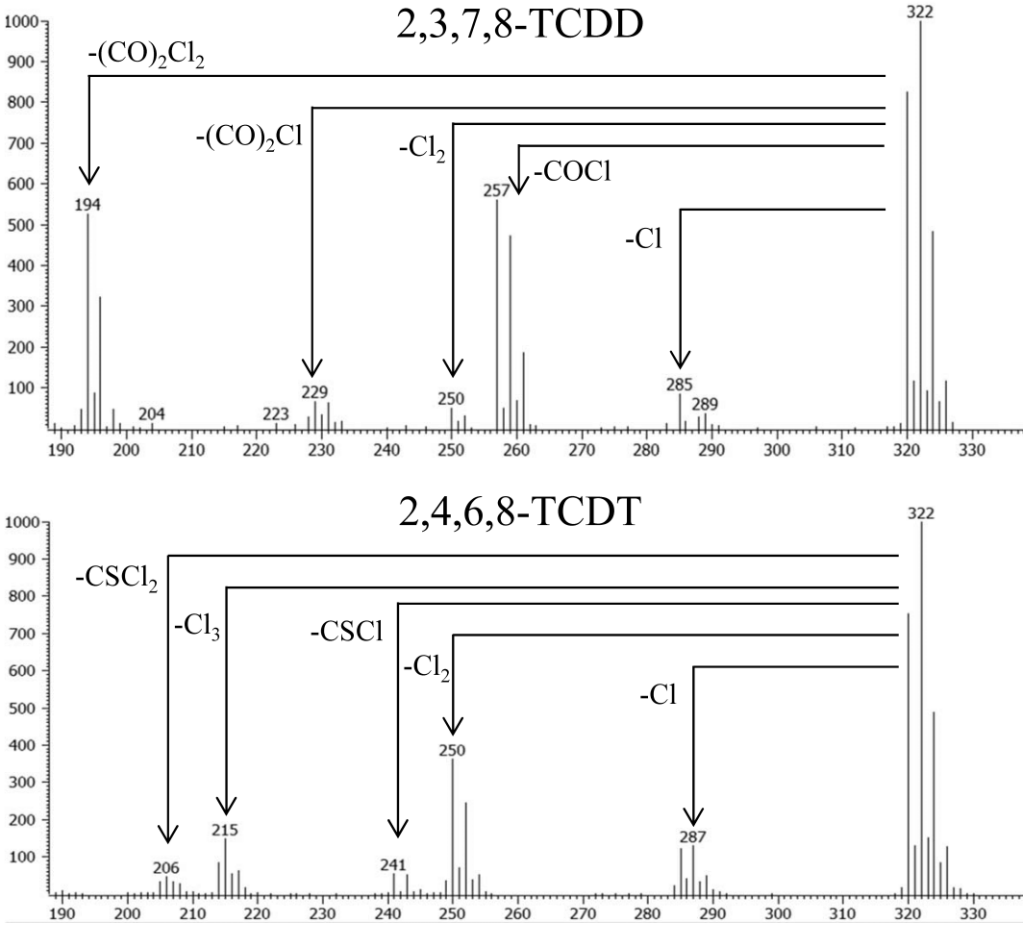

Figure 1. EI mass spectra of 2,3,7,8-TCDD (top) and 2,4,6,8-TCDT (bottom).

Considering the chromatography of the pair of compounds, 2,4,6,8-TCDT was found to elute close to the tetrachlorodibezno-p-dioxin isomer elution window. To help resolve the compounds, an RTX-Dioxin2 column was used for the first dimension separation in the GCxGC-TOFMS analyses. This column is known to provide improved separation of the chloro-dioxins and furans. Therefore, 2,4,6,8-TCDT was easily resolved from the closest tetrachloro dioxin isomer (1,2,8,9-TCDD), which historically has caused misidentifications. The GCxGC-TOFMS separation of the tetrachloro dioxins and 2,4,6,8-TCDT can be observed in Figure 2.

GCxGC-TOFMS analysis was performed on the sediment samples and, using isotope dilution, an initial quantification of the samples was performed. All of the 17 WHO regulated tetra through octa chlorinated dioxins and furans were quantified in the samples.

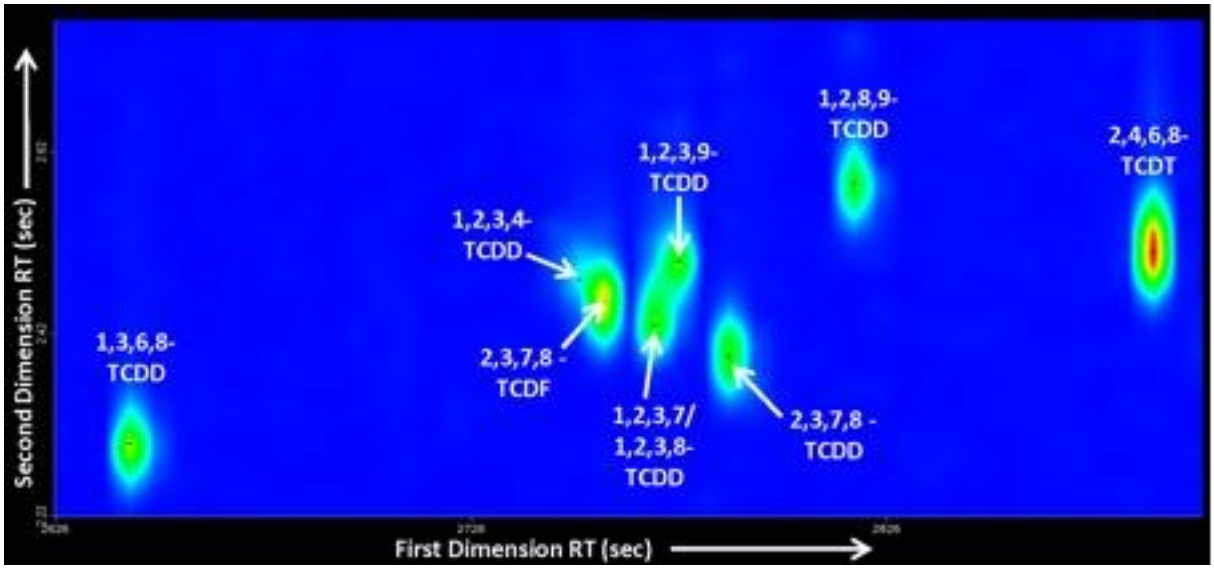

Figure 2. Two dimensional contour chromatogram demonstrating the resolution of 2,4,6,8-TCDT from the tetrachloro dibenzo-p-dioxins.

The levels of the dioxins, furans, and dibenzothiophenes were not high enough in all of the river sediments to be observed using the TOF-MS. Therefore, the river sediment extracts were also analyzed with the APGC-TQ-S. This analysis was also performed for more accurate quantitation. Selective MRM transitions were developed for each compound, and again, the two groups of compounds were resolved from one another (Figure 3).