Method Development for Analysis of PCDD from Simulated Dechlorination Reactions by Sediment Derived Microorganisms

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Introduction

Methods for the clean-up and analysis of tetra- to octa-chlorinated dioxins and dibenzofurans are well documented in the literature. The obvious reason for the extent of this documentation is the higher toxicity of tetra- to octa-chlorinated dibenzo-p-dioxins (CDD) and chlorinated dibenzofurans (CDF). Various routes for the formation of polychlorinated dibenzo-p-dioxins (PCDD) indicate that the formation of toxic PCDD (tetra- to octa-CDD) occurs from chlorination of unchlorinated and mono- to tri-chlorinated dibenzodioxins or various precursors. It has also been reported that dechlorination of octa- to tetra -CDD results in the formation of mono- to tri-CDD. Lower chlorinated dioxins, mono- to tri-CDD, are involved in the formation of toxic, tetra- to octa-CDD. Thus, for the mechanistic studies of formation of and dechlorination of PCDD it is important to analyze the samples for mono- to octa-CDD. The analytical task becomes challenging when samples contain interfering compounds. Currently available methods are not completely satisfactory for the clean-up and analysis of mono- to tri-CDD and total -CDD in complicated samples.

Laboratory experiments have shown that PCDD/F undergo dechlorination in contaminated water by sediment derived microorganisms under reduced anaerobic conditions (1). Moreover it was also shown that 2,3,7,8-Tetra CDD can be dechlorinated to non-toxic mono-, di- and tri-CDD (2). To understand the mechanism of dechlorination by microorganisms under anaerobic conditions it was necessary to develop a method for analysis of mono- to octa-CDD. In the current investigation simulated reactions of dechlorination were conducted using highly contaminated river sediment. The clean-up procedures reported for tetra- to octa-CDD were

modified to suit the separation and isolation of mono- to tri-CDD. Special GC capillary columns were used to analyze mono- to tri-CDD in addition to the analysis of tetra- to octa –CDD.

Material and Methods

Highly contaminated river sediment samples were treated under reduced anaerobic conditions using microorganisms. The sediment treatment involved triplicate samples of a) control samples, b) the samples with addition of bromodioxins, and c) the samples with addition of hydrogen. After an incubation of three months, sample preparation, clean-up and analysis were conducted for all samples. In a typical procedure, an air-dried sample (25 g) was spiked with 13C-PCDD and then Soxhlet extracted for 48 h using toluene. Extracts were concentrated and cleaned using modified EPA Method 1613.

HP5890/5972A GC -MSD and HP5880 GC-ECD instruments were used for the analysis of the samples. ICB-1, 30 m x 0.25 mm, 0.25 μm film, ICB-5, 30 m x 0.25 mm, film 0.25 um, Liquid Crystal LC-50, 10 m x 0.25 mm, film 0.2 μm, and Liquid Crystal LC-50, 30 m x 0.25 mm, film 0.125 μm were used for the analysis (3, 4).

Results and Discussion:

It is observed that in spite of the use of extensive clean-up, it is impossible to remove all chlorinated interfering compounds, especially interferences in mono- to tri-CDD. EPA Method 1613 is useful for tetra- to octa-CDD. In the current investigation the method is modified to collect a fraction containing mono- to tri-CDD, in addition to tetra- to octa-CDD. It was observed that the fraction containing mono- to tri-CDD was loaded with interfering compounds. For further simplification of separation and analysis, the samples were analyzed using different capillary columns in gas chromatography. The liquid crystal column used shows the separation of individual isomeric CDD better than their separation on regular columns such as ICB-1 and ICB-5. The separation of mono- to tri-CDD on the liquid crystal (LC-50) column and ICB-5 column is shown in Figure 1 and Figure 2, respectively. Thus, a method is developed for the analysis of mono- to octa-CDD using modified EPA Method 1613 and using two different capillary columns.

References:

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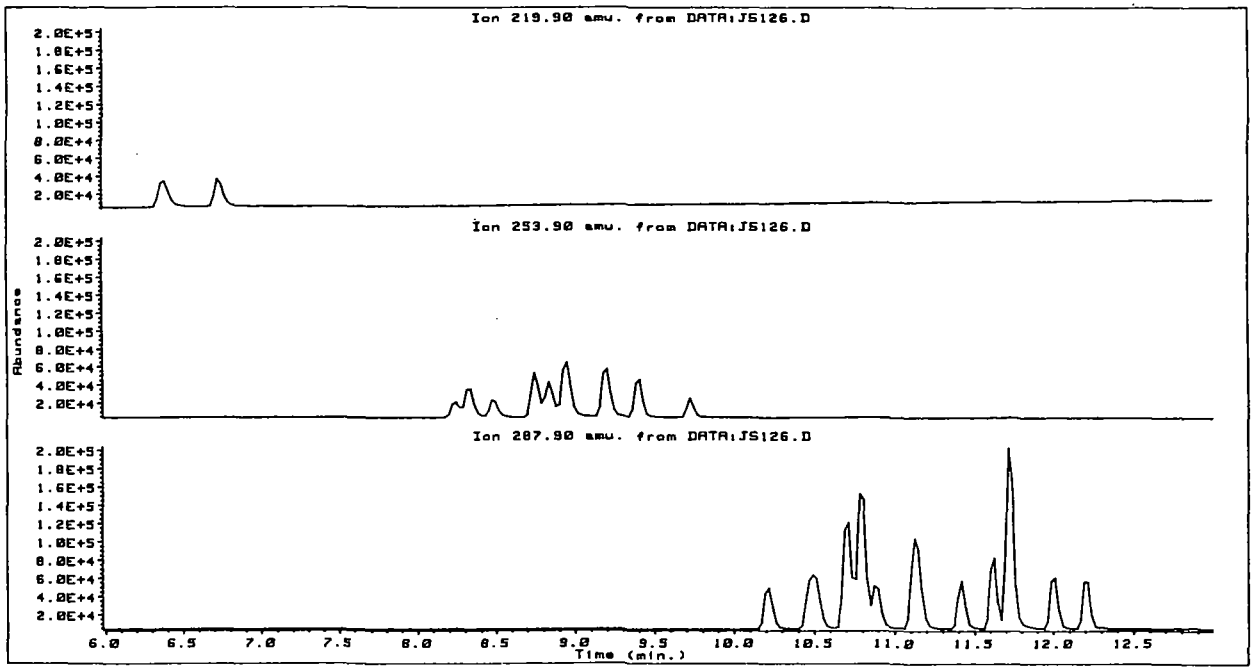

Figure 1: GC-MSD SIM Traces for mono-CDD, di-CDD, and tri-CDD in a PCDD mixture. Column LC-50, 10m x 0.25mm I.D., 0.2µm film. Temperature program: 100°C for 1 min., programmed to 240°C @ 10°C/min, then programmed to 275°C @ 4°C/min, 20 min at 275°C.

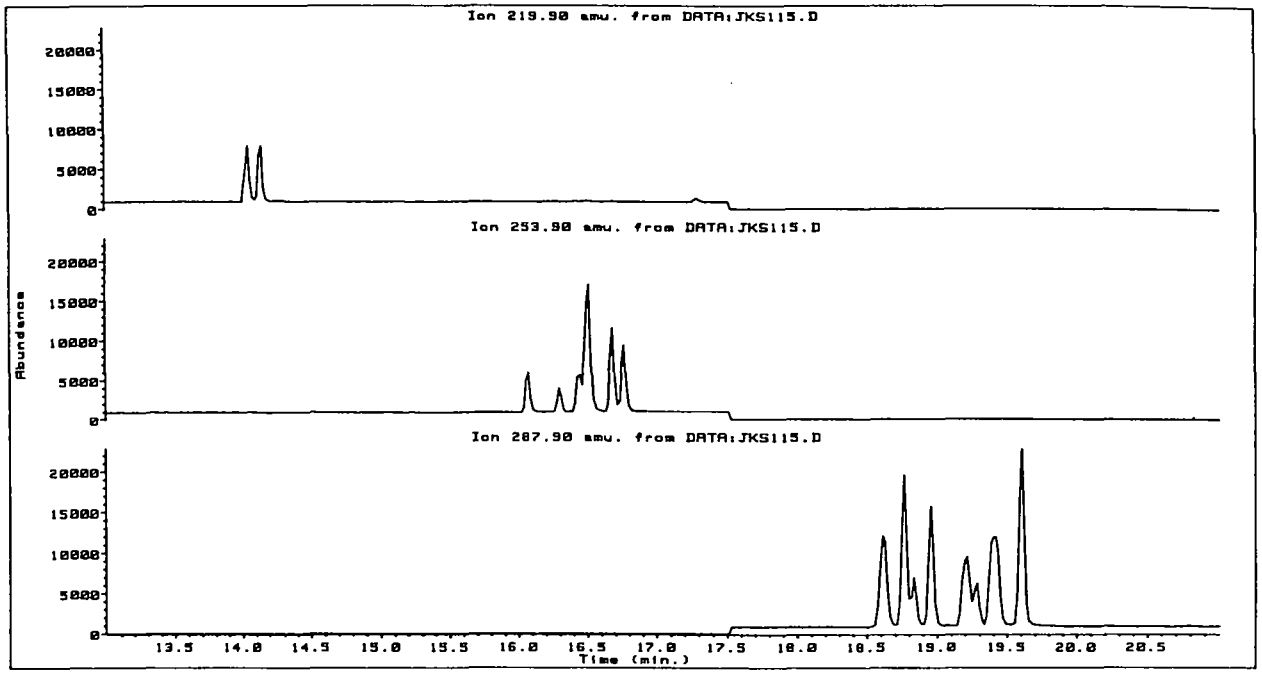

Figure 2: GC-MSD SIM Traces for mono-CDD, di-CDD, and tri-CDD in a PCDD mixture. Column ICB-5, 30m x 0.25mm I.D., 0.25μm film. Temperature program: 80°C for 1 min., programmed to 210°C @ 10°C/min, then programmed to 300°C @ 5°C/min, 20 min at 300°C.