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Selective separation of fluorinated compounds from complex organic mixtures by pyrolysis-comprehensive two-dimensional gas chromatography coupled to high-resolution time-of-flight mass spectrometry

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ABSTRACT

The usefulness of comprehensive two-dimensional gas chromatography (GC × GC) was demonstrated for the selective separation of fluorinated compounds from organic mixtures, such as kerosene/perfluorokerosene mixtures, pyrolysis products derived from polyethylene/ethylene-tetrafluoroethylene alternating copolymer mixture and poly[2-(perfluorohexyl)ethyl acrylate]. Perfluorocarbons were completely separated from hydrocarbons in the two-dimensional chromatogram. Fluorohydrocarbons in the pyrolysis products of polyethylene/ethylene-tetrafluoroethylene alternating copolymer mixture were selectively isolated from their hydrocarbon counterparts and regularly arranged according to their chain length and fluorine content in the two-dimensional chromatogram. A reliable structural analysis of the fluorohydrocarbons was achieved by combining effective GC × GC positional information with accurate mass spectral data obtained by high-resolution time-of-flight mass spectrometry (HRTOF-MS). 2-(Perfluorohexyl)ethyl acrylate monomer, dimer, and trimer as well as 2-(perfluorohexyl)ethyl alcohol in poly[2-(perfluorohexyl)ethyl acrylate] pyrolysis products were detected in the bottommost part of the two-dimensional chromatogram with separation from hydrocarbons possessing terminal structure information about the polymer, such as α-methylstyrene. Pyrolysis-GC × GC/HRTOF-MS appeared particularly suitable for the characterization of fluorinated polymer microstructures, such as monomer sequences and terminal groups.

1. Introduction

In recent years, fluorinated compounds have rapidly emerged as attractive substances for many fields, such as coatings, lubricants, films, electric materials, optical materials, refrigerants, food containers, analytical reagents, medical devices, and pharmaceuticals [1–5]. A variety of these compounds have widely spread throughout the environment, including in wildlife and humans [6–9]. Their selective separation from highly complex organic mixtures, such as biological tissues, environmental samples, and polymer pyrolysis products, is crucial to understanding their pharmacokinetics, environmental fate, and structure–property relationship [6–9]. Although pyrolysis (Py)-gas chromatography (GC)/mass spectrometry (MS) is often used to structurally characterize polymers, including fluorinated polymers [10–12], the pyrolysis of fluorinated polymers often generates highly complex organic mixtures that cannot be completely resolved by conventional one-dimensional (1D) GC [11,13].

Over the past decades, comprehensive two-dimensional gas chromatography (GC × GC) has been developed and applied to separate highly complex organic mixtures, such as petroleum, geochemical, and environmental samples [14–18]. Its separation ability is several tens of times higher than 1D GC. In addition to an enhanced separation, it facilitates analyte identification because organic compounds are detected in an orderly fashion according to their volatility and polarity in the two-dimensional (2D) chromatogram. Furthermore, its coupling with high-resolution time-of-flight mass spectrometry (HRTOF-MS) has proven a very powerful analytical approach for complex organic mixtures [14,16,19]. Few reports have addressed GC × GC analyses of fluorinated compounds. Korytár et al. have reported that mono- and di-fluorinated brominated diphenyl ethers (BDEs) can be separated

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