Determining indicator toxaphene congeners in soil using comprehensive two-dimensional gas chromatography–tandem mass spectrometry

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ARTICLE INFO

ABSTRACT

Toxaphene, which is a broad spectrum chlorinated pesticide, is a complex mixture of several hundred congeners, mainly polychlorinated bornanes. Quantifying toxaphene in environmental samples is difficult because of its complexity, and because each congener has a different response factor. Toxaphene chromatograms acquired using one-dimensional gas chromatography (1DGC) show that this technique cannot be used to separate all of the toxaphene congeners. We developed and validated a sensitive and quantitative method for determining three indicator toxaphene congeners in soil using an isotope dilution/comprehensive two-dimensional gas chromatography–tandem mass spectrometry (GC × GC–MS). The samples were extracted using accelerated solvent extraction, and then the extracts were purified using silica gel columns. $^{13}C_{10}$-labeled Parlar 26 and 50 were used as internal standards and $^{13}C_{10}$-labeled Parlar 62 was used as an injection standard. The sample extraction and purification treatments and the GC × GC–MS parameters were optimized. Subsequently the samples were determined by GC × GC–MS. The limits of detection for Parlar 26, 50, and 62 were 0.6 pg/g, 0.4 pg/g, and 1.0 pg/g ($S/N=3$), respectively, and the calibration curves had good linear correlations between 50 and 1000 μg/L ($r^2 > 0.99$). Comprehensive two-dimensional GC gave substantial improvements over one-dimensional GC in the toxaphene analysis. We analyzed soil samples containing trace quantities of toxaphene to demonstrate that the developed method could be used to analyze toxaphene in environmental samples.

1. Introduction

Toxaphene is a complex mixture that primarily consists of chlorinated bornanes, with some chlorinated camphenes, dihydrocamphenes, bornenes, and bornadienes [1]. The number of theoretically possible polychlorinated bornane congeners is 32,768, most of which are chiral [2]. Toxaphene was first produced in the United States by the Hercules Powder Company in the mid-1940s, and was widely used as an insecticide on cotton, soybean, and corn crops [3]. Toxaphene was the most applied pesticide in the USA and other countries in the mid-1970s. The total global production has been estimated to be $0.45 - 1.33 \times 10^6$ t [1], of which 2.0×10^4 t were produced in China. Toxaphene congeners are ubiquitous in the environment [4] because of their widespread

use and environmental stability, and they have been found worldwide in air, soil, and biota (including aquatic organisms, particularly marine mammals, such as beluga whales) [5–11]. The use of toxaphene was restricted in the 1980s because of its toxicity, and persistence, and because of its potential to bioaccumulation and undergo long-range transport [8,12]; and it is classed as a persistent organic pollutant (POPs) under the Stockholm Convention [13].

The analysis of toxaphene is a difficult task because of the complexity of the commercial mixtures and the lack of quantification standards. Up to now, a number of types of instrumentation and analytical methods have been used to quantify toxaphene in environmental samples. Toxaphene can be analyzed using gas chromatography (GC) with an electron capture detector (ECD), but the preferred detector is currently a mass spectrometer (MS) because of the selectivity and sensitivity that can be achieved [3,14]. Each of these detectors has both advantages and inherent problems. GC-ECD offers high sensitivity and low costs, but it is

equally selective for toxaphene compounds and other organochlorine compounds, leading to the possibility of concentrations being overestimated because of interferences. Another drawback is that GC-ECD analysis cannot give information on the toxaphene congener composition in a sample. In contrast, the MS detection is based on the mass-to-charge ratios of the ionized compounds, but in this case, the fragmentation of the molecular ion provided the main differences of the response factor of the target ion [8]. High resolution GC has been used to study the composition of technical toxaphene, but it is not possible to satisfactorily separate the toxaphene congeners even with the separation performance that can be achieved using this technique. To overcome these problems, tandem MS [8,15,16] and high resolution MS [17,18] have been used to determine toxaphene separated using GC, but these techniques still cannot provide accurate quantification or effective separation of the complicated toxaphene mixtures.

In the analysis of trace pollutants in environmental samples, it is a challenge to extract target analytes that are present at very low concentrations and separate them from complex matrices. It is, therefore, very difficult to quantify toxaphene residues in environmental matrices accurately using common methods. Most of the problems in this analysis are caused by the complexity of the original toxaphene mixture, interference by other organohalogen compounds and/or matrix constituents, and the very different concentrations of compounds that co-elute in the clean-up procedures. Comprehensive two-dimensional GC (GC × GC) can be used to solve these problems because it is an extremely powerful separation technique in which two GC columns, with different separation mechanisms, are connected using an interface called a modulator [13,19]. GC × GC has a higher analyte capacity and potential resolving power than conventional one-dimensional (1D) GC [20]. GC × GC has been successfully used to analyze POPs in complex samples [13,21–25].

Although there are a large number of toxaphene congeners, it has been shown that the congeners Parlar 26, Parlar 50, and Parlar 62 (Fig. 1) are predominate congeners. The sum of the concentration of these three compounds normally being approximately 8–50% of the total toxaphene concentration, and these are called indicator toxaphene congeners [17]. In the document "Guidance on the Global Monitoring Plan for Persistent Organic Pollutants" published in 2007 [26], it was suggested that the toxaphene congeners Parlar 26, 50, and 62 should be analyzed in environmental media. However, to the best of our knowledge, "total" toxaphene, using a technical toxaphene standard as a reference, has been measured and reported in most studies [11], most of which have been focused on aquatic organisms. Few reports of concentrations of the toxaphene indicator congeners in soil samples are available in the open literature. Moreover, the methods used in most of the studies that have been published have not

involved using isotope-labeled internal standards that was to avoid matrix effects when analyzing real environmental sample extracts. Because of the problems outlined above, it is critical that a robust, sensitive analytical method for determining the toxaphene indicator congeners at trace concentrations in soil samples is developed.

The objective of the research described here was to assess the feasibility of using GC × GC–MS to accurately determine the toxaphene indicator congeners Parlar 26, 50, and 62 in typical soil samples. Different initial temperatures, injection modes, gas flow rates, and other instrumental parameters were evaluated and the optimum combination of parameters was selected. The sample preparation (i.e., extraction and cleanup) techniques were also evaluated and optimized. Soil samples were then analyzed for the indicator toxaphene congeners using the optimized method, and the results were compared with the results of analyzing the same extracts using other methods.

2. Materials and methods

2.1. Chemicals and reagents

Pesticide analysis grade acetone, n-hexane, methanol, and dichloromethane (DCM) were purchased from J. T. Baker (Phillipsburg, NJ, USA) and nonane was purchased from Sigma (St. Louis, MO, USA). Silica gel (100–200 μm), concentrated H_2SO_4, and anhydrous Na_2SO_4 were "guaranteed reagents" (minimum 99.8% pure), purchased from local manufacturers. Anhydrous Na_2SO_4 was dried at 660 °C for 7 h before use, and the silica gel was cleaned with dichloromethane and methanol, dried at 35 °C for 12 h, then activated at 550 °C for 7 h. Acidified silica gel was prepared by adding 44 g H_2SO_4 to 56 g activated silica gel (44% w/w) or 22 g H_2SO_4 to 78 g activated silica gel (22% w/w). Standard solutions of Parlar 26 (ULM-7828), Parlar 50 (ULM-7829), Parlar 62 (ULM-7830), $^{13}C_{10}$-Parlar 26 (CLM-7930), $^{13}C_{10}$-Parlar 50 (CLM-7931), and $^{13}C_{10}$-Parlar 62 (CLM-7932) were obtained from Cambridge Isotope Laboratories (Andover, MA, USA). Technical toxaphene was purchased from Dr. Ehrenstorfer (Augsburg, Germany).

2.2. Sample extraction

Soil sample was collected from an area in China that was not polluted with toxaphene, and the toxaphene congener concentrations in the soil were found to be below the detection limits. The sample was freeze-dried and homogenized by passing it through a stainless steel 80-mesh sieve. The analysis procedure involved extracting the toxaphene congeners from the sample, then purifying and concentrating the extract before instrumental analysis.
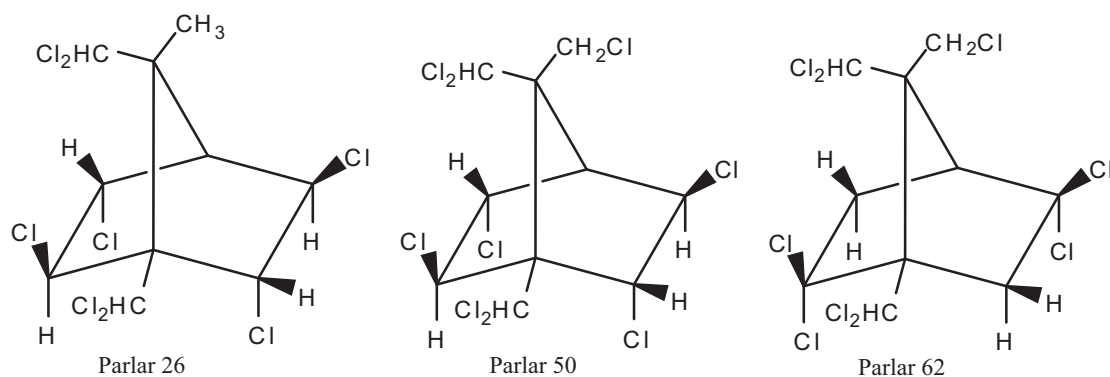

Fig. 1. Chemical structures of the indicator toxaphene congeners.