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Short communication

Determination of JP-8 components in soils using solid-phase microextraction–gas chromatography–mass spectrometry

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Abstract

Jet Propellant-8 (JP-8) is a military fuel associated with a large percentage of chemical exposures documented by the US Department of Defense. A fast and sensitive solid-phase microextraction–gas chromatographic–mass spectrometric (SPME–GC–MS) method has been developed for the determination of 34 'marker compounds' found in JP-8. Linear ranges ($R^2 > 0.99$) were determined for each marker component and precision was measured (<16% RSD) for these components over four concentrations within each calibration range. The method was applied for the analysis of JP-8 components from soil. The use of SPME over other sample extraction techniques eliminates solvents, minimizes sample handling, and increases sensitivity.

Keywords: JP-8; Jet fuel; GC–MS; SPME

1. Introduction

Several kerosene based fuels designated JP (Jet Propellant) are currently in use by the United States military and other North Atlantic Treaty Organization (NATO) countries. These fuels are given classifications such as JP-8, which characterizes land based aircraft fuel [1], JP-5, sea based fuel [2], or JP-10, which defines a synthetic fuel used in rockets [3]. JP-8 is the primary aircraft fuel used by the US military with an annual consumption of 2.5 million gallons per year [4,5]. JP-8 is composed of hundreds of organic compounds, primarily *n*-alkanes, *iso*-alkanes, aromatics, and polycyclic aromatic hydrocarbons [5]. Some of these components, including benzene and naphthalene, are known carcinogens [5,6] while others (namely C_{10}–C_{16} *n*-alkanes) are known to increase the carcinogenic potential of other JP-8 components [7].

A recent review article summarizes the available methods for JP-8 analysis (or analysis of subsets of JP-8 components) [8]. Liquid–liquid extraction (LLE) is a popular pretreatment for GC–MS determination of JP-8 components from environmental and biological matrices [8–10]. Although effective, LLE is time-consuming, requires extensive sample handling, and utilizes solvents. Solid-phase microextraction (SPME) provides a solvent-free alternative to LLE and has gained increasing acceptance in the field of VOC (volatile organic compound) analysis [8]. SPME utilizes a fiber coated with GC column material, typically PDMS (polydimethylsiloxane), which is inserted into the sample or sample headspace to adsorb the analyte(s). The analyte(s) are subsequently desorbed into the GC injection port [11]. SPME has shown to have comparable or better recovery than LLE but requires no solvents and no sample handling beyond introduction of the soil sample into the vial [12,13].

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Table 1
Marker components monitored from JP-8 fuel with limits of detection (LOD) in ppb

Aliphatic hydrocarbons	Aromatic hydrocarbons	Cyclic alkanes	Naphthalenes
2-Methylheptane (100)	Toluene (10)	Methylcyclohexane (200)	Naphthalene (0.02)
n-Octane (100)	Ethylbenzene (20)	*cis*-1,3-Dimethylcyclohexane (50)	1-Methylnaphthalene (0.02)
n-Nonane (20)	Xylenes (20)	*cis*-1,2-Dimethylcyclohexane (50)	
2-Methylnonane (5)	*n*-Propylbenzene (20)	*trans*-1,3-Dimethylcyclohexane (50)	2-Methylnaphthalene (0.02)
n-Decane (1)	2- & 3- Ethyltoluene (5)	*trans*-1,2-Dimethylcyclohexane (50)	
n-Undecane (0.5)	1,3,5-Trimethylbenzene (5)	*n*-Propylcyclohexane (5)	
n-Dodecane (0.05)	1,2,4-Trimethylbenzene (5)	*n*-Butylcyclohexane (1)	
n-Tridecane (0.05)	1,3-Diethylbenzene (1)		
n-Tetradecane (0.05)	1,4-Diethylbenzene (1)		
n-Pentadecane (0.05)			
n-Hexadecane (0.05)			
n-Heptadecane (0.05)			
n-Octadecane (0.05)			

SPME–GC–MS has been previously used to monitor alkanes and small subsets of hydrocarbons (including BTEX – benzene, toluene, ethyltoluene, and xylenes) from water, soil and blood [14–17]. This project focuses on developing a SMPE–GC–MS method to determine the presence of JP-8 in soil by tracking 34 marker compounds (Table 1). This approach of using a set of marker compounds has been utilized by regulatory agencies for the clean-up of weathered petroleum waste and was recently proposed as a viable option to evaluate toxicity of this complex mixture [4]. This approach, referred to as the surrogate hydrocarbon mixture (SHM), has also been utilized to examine JP-8 aerosol exposures [18]. Monitoring JP-8 by SPME–GC–MS may find applications in the Department of Defense as exposure to JP-8 accounts for the largest percentage of all chemical exposures reported by this agency [5,8]. Accidental releases account for most of the JP-8 exposure to the environment [19]. The SPME–GC–MS method presented here was evaluated for precision, represented by % relative standard deviation (%RSD), and for linearity of each marker component within its calibration range.

2. Experimental

2.1. Materials and instrumentation

A standard solution containing each marker component (1000 μg/mL) was ordered from Restek (Bellefonte, PA). Ethyl acetate and I-Chem jars (certified VOC free) were purchased from Fisher Scientific (Pittsburgh, PA). The JP-8 fuel was donated by the Defense Logistics Agency (North Charleston, SC). All experiments were completed on a ThermoFinnigan Trace GC with Polaris Q (ion trap) Mass Spectrometer (Thermo Electron Corporation, Waltham, MA). The separation was performed on a VF-5ht column (30 m, 0.25 mm i.d., 0.10 μm film thickness) (Varian, Lake Forest, CA). Automatic sampling was made possible by the LEAP CombiPAL (LEAP Technologies, Carrboro, NC). Fibers composed of 100 μm PDMS were purchased from Supelco (Milwaukee, WI). Each fiber was used for approximately 200 injections. Gas-tight autosampler vials (20 mL) were obtained through Microliter Analytical (Suwanee, GA).

2.2. SPME–GC–MS method

The SPME–GC–MS method was optimized for maximum peak area and peak symmetry. The SPME conditions optimized included extraction time (2, 5, 10, 15, 20, and 25 min), extraction temperature (50, 70, 90, and 100 °C), desorption time (0.5, 1, 1.5, 3, and 5 min) and desorption temperature (200, 225, and 250 °C). The final SPME conditions for soil analysis involved a 1 g soil sample with a 90 °C extraction for 20 min [20]. The fiber was allowed to desorb in the GC injection port for 1.5 min at 250 °C [20]. The GC was programmed to maintain 40 °C for 3 min followed by a temperature gradient of 40–250 °C at 10 °C/min [20]. All samples were run in full scan mode with electron ionization (EI). Because of the complexity of the total ion chromatograms, extracted ion chromatograms were used for sample processing. During the method development phase, characteristic ions were identified to extract peaks from the various hydrocarbon types. Aliphatic hydrocarbons were monitored with *m/z* 57, 71, 85, and 99. Aromatic hydrocarbons were monitored using *m/z* 77, 79, 91, 92, 106, and 120. Cyclic alkanes were monitored with *m/z* 82, 97, 111, 112, and 140 while naphthalene compounds were followed using *m/z* 115, 128, 141, 142, and 156. Because of the similarity in the mass spectra of several compounds within an analyte group, the identities of each component were verified in the custom standard and in the JP-8 sample by matching retention times with references standards and matching mass spectra using the EI library provided by Thermo Finnigan.

2.3. Calibration and precision

Stock solutions of 100, 10, 1, 0.1 and 0.01 μg/mL were made from the custom standard (1000 μg/mL of each marker component) in ethyl acetate. Calibration curve solutions with concentrations ranging from 1 μg/mL to

Table 2
Linearity (R^2) and precision (%RSD) for each set of JP-8 marker components

Component type	Average R^2 ($n > 5$)	Average %RSD*
Aliphatic hydrocarbons	0.9941	13.63
Aromatic hydrocarbons	0.9939	12.26
Cyclic alkanes	0.9918	15.18
Naphthalenes	0.9970	11.77

* $n = 5$ Replicates each at four different concentrations.

0.00002 μg/mL were also prepared in ethyl acetate. Each calibration curve contained at least five points with each point prepared in triplicate. The actual range of the curve for each marker component varied with individual sensitivities. Table 1 shows the limit of detection (LOD) for each marker component as determined by a 3:1 signal to noise ratio. To test the reproducibility of the method, an analysis was performed on five replicates of four different concentrations within the calibration range of each component. The concentrations chosen for this experiment included the high and low points of each calibration range plus two additional points within the range. Precision was represented as % relative standard deviation (%RSD). The linearity and precision data are summarized in Table 2.

2.4. Method application

This SPME–GC–MS method had been previously applied in an 'ideal' soil matrix (sand), but it was anticipated that more environmentally relevant soil may affect SPME extraction [20]. To test this, soil samples from the Charleston Air Force Base and sites within a 10 mile radius of the base were collected. The CAFB was chosen based on its proximity to the research site and not because of any suspected contamination. Each site yielded approximately 160 g of sample soil, by use of a handheld core sampler. Following collection, samples were stored frozen in sealed freezer bags. Baseline samples of these soils were analyzed to determine if they contained any of the marker components. Following this initial SPME–GC–MS analysis, the samples were dried at 150 °C for one week.

A set of three microcosms were prepared for each soil sampling site. The microcosms were made in 500 mL I-Chem glass jars that were certified free of volatile organic compounds. Each sample location was broken down into three microcosms: one control, one spiked with JP-8 fuel (5 mL of 1:100 dilution in ethyl acetate), and one spiked with a standard (5 mL of 100 μg/mL standard), each containing approximately 50 g of soil. The samples were then shaken and allowed to sit sealed for 24 h to allow equilibrium to establish inside each jar. After the 24 h elapsed, the jars were opened and three 1 g samples of each soil were removed for GC–MS analysis. Jars were kept open to allow for evaporation in a climate controlled room (22 °C). Additional samples were pulled for analysis at 2, 3, 4, 5, 8, and 15 days post-exposure.

3. Results and discussion

The GC–MS method was first developed for liquid samples and then optimized to incorporate SPME technology [13]. The use of SPME lowered the detection limit for most of the components of interest and eliminated the need for liquid–liquid extraction. The final extraction conditions included a 20 min extraction at 90 °C. There was no statistically significant difference between 20 and 25 min extractions, so the smaller amount of time was chosen. The same was true for the 90 °C extraction versus 100 °C. The extraction of the analytes can be affected by the characteristics of the coating, the temperature and time of the extraction process, the addition of salt or an organic solvent to the sample, pH modification, agitation of the sample, and the sample volume [11]. Due to the non-polar nature of the JP-8 components being tested, pH modification was unnecessary. Additionally, since the components were volatile enough to efficiently transition into the headspace, addition of an organic solvent was also not necessary. Headspace SPME sampling (HSSPME) is consistent with other literature methods for analysis of complex matrices [12,14–17]. The non-polar PDMS fiber was chosen because of its affinity for the JP-8 marker components. The 100 μm coating on the fiber ensured maximum adsorption sites, but required the highest allowable desorption temperature (250 °C) to thoroughly remove all of the analytes. Maximum desorption occurred after 1.5 min without compromised peak shape. Maximizing desorption time and temperature will serve to minimize carry-over [11].

The GC–MS data was collected in full scan mode since the use of multiple ions for SIM (Selected Ion Monitoring) would have compromised sensitivity. The peaks of interest were isolated using an extracted ion chromatogram technique in the GC–MS software. For example, all of the aliphatic hydrocarbons had the same MS fragmentation pattern, so this series of m/z (mass-to-charge) ratios could be used to isolate all of those peaks which also helped simplify the data interpretation. Within each extracted ion chromatogram, all analytes were baseline resolved. The identity of each marker component was further verified with a retention time match to a standard chromatogram and a mass spectral match from a reference library. The use of extracted ion chromatograms also helped keep the run time reasonably short (24 min for analysis of 34 components).

The method proved to have acceptable linearity and precision within each marker component's calibration range (Table 2). The calibration ranges varied for each component based on different sensitivities (which were dictated by different affinities for the SPME fiber). For example, smaller more volatile compounds had higher limits of detection. Due to the non-polar nature of the SPME fiber coating, the smaller more volatile components were often out competed for SPME adsorption sites. Nevertheless, each marker component could be detected at sub-ppm levels. The method also proved to be reproducible (Table 2)

over four different concentrations within each calibration range.

Soil samples were spiked with JP-8 and the reference standard to monitor the evaporation of the marker components over time (Fig. 1). None of the soils collected showed any baseline concentrations of the JP-8 components. After spiking the soils in our microcosm experiments, we noticed a significant drop (>75%) for most marker component concentrations within the first 48 h. The naphthalene compounds had the slowest evaporation (~35% within first 48 h in JP-8 sample in ~50% in standard sample). After 15 days, none of the marker components were at detectable levels in the microcosms. In general, the rate of evaporation from soils will vary based on soil type, moisture content, and weather conditions.

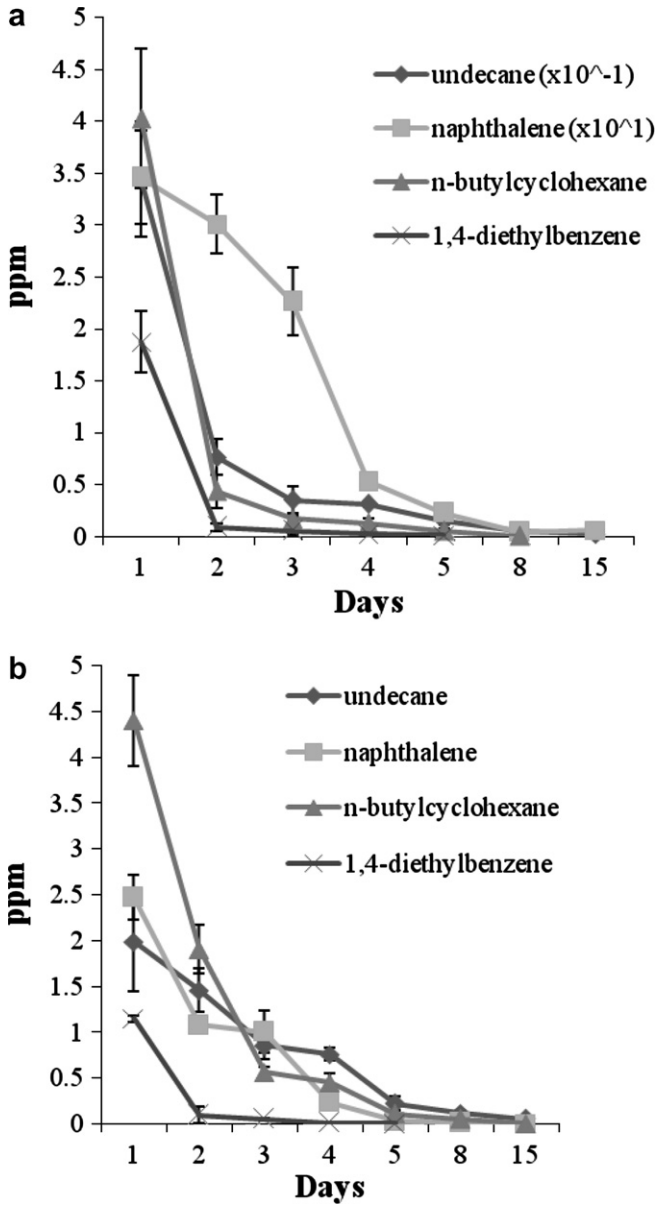

Fig. 1. Evaporation trend for selected JP-8 components from Charleston Air Force base soil ($n = 3$ at each data point): (a) soil sample spiked with JP-8 (b) soil sample spiked with standard hydrocarbon mixture.

4. Conclusions

A method for determining 34 different marker components from JP-8 fuel has been developed and tested in soil. The method involves a SPME extraction which allows for direct sampling into the SPME vial and eliminates the need for toxic extraction solvents. The use of SPME as a sampling and extraction tool helps minimize the chance for sample contamination both from sample handlers and from solvents commonly used for LLE. The separation is performed using GC, which is the benchmark technology for volatile compound analysis because the separation is based on differences in boiling points. The use of mass spectrometry as a detector provides added sensitivity over other GC detectors and provides reassurance of compound identification with the help of extracted ion chromatograms. The method shows good linearity, sensitivity, and precision for all 34 marker components. The method has been applied to a small scale soil experiment where JP-8 marker components were monitored for 2 weeks post-exposure to the soil. This method represents a fast, inexpensive, solvent-less way to screen for the presence of JP-8 at possible contaminated sites and could provide a first point of reference for documenting accidental JP-8 exposures in the environment.

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