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## DEVELOPING A SOLID PHASE MICROEXTRACTION METHOD FOR THE IDENTIFICATION OF ACCELERANTS IN FIRE DEBRIS

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### ABSTRACT

*Solid Phase Microextraction (SPME) method of identifying accelerants from fire debris is developed. Experimental design methodology was used to evaluate the simultaneous effect of SPME operating variables (extraction time, extraction temperature, desorption time) on the extraction of target analytes (benzene, toluene, xylene and hexadecane). The results showed that extraction temperature and extraction time were the more significant factors. Optimum operating conditions for SPME were determined using a response surface method. The results indicate that SPME is capable of analyzing accelerants from fire debris.*

*Keywords: solid phase microextraction, accelerants, fire debris*

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### 1. INTRODUCTION

In most cases involving arson, accelerants such as gasoline, kerosene, and paint thinner are used because of their low cost and easy availability<sup>1</sup>. An important aspect of an investigation of a suspected arson case involves the chemical analysis of the debris remaining after the fire<sup>2</sup>. Visual pattern recognition can be employed to confirm the identification of an unknown accelerant<sup>1</sup>. In this study, a solid phase microextraction (SPME)

method coupled to gas chromatography flame ionization detector was developed for analyzing the profile of several types of accelerants. The simplicity of operation, sensitivity, selectivity, portability, and the solvent-free nature of the SPME method make it a powerful tool for sample introduction method for gas chromatographic analyses of organic chemicals<sup>3</sup>. It is based on the enrichment of analytes on a polymer or adsorbent-coated fused-silica fiber either directly to the sample or its headspace. The extraction efficiency of SPME technique

is dependent on several experimental parameters such as the extraction time, extraction temperature and desorption time<sup>4,5</sup>. In this study, the operating parameters were optimized using an experimental design approach that consisted of three stages; identifying the factors which may affect the result of an experiment, designing the experiment so that the effects of uncontrolled factors are minimized, and using statistical analysis to separate and evaluate the effects of the various factors involved<sup>6</sup>.

## 2. EXPERIMENTAL METHODS

### 2.1 SPME Procedure

SPME extractions were performed using 100  $\mu\text{m}$  polydimethylsiloxane (PDMS) fiber (Supelco, Bellefonte, Pennsylvania, USA). The fiber was conditioned in a gas chromatograph injection port at 250  $^{\circ}\text{C}$  to remove fiber contaminants as recommended by the manufacturer. A 2 ml volume of sample was added to a 5 ml glass vial and heated to a specific temperature depending on the experiment. Then, the SPME fiber was exposed to the headspace of the vial. The solution was stirred with a magnetic stirrer (0.8 cm x 0.2 cm). After extraction, the fiber was withdrawn into the needle, pulled out from the vial and immediately injected into the GC.

### 2.2 Sample Preparation

Wood chips were placed into a 25 ml Erlenmeyer flask. The chosen accelerant was poured into the 25 ml Erlenmeyer flask to cover the chips completely. The flask was capped with rubber septa and the chips were left to soak for about four to six hours. After soaking the chips, the excess accelerants were poured out of the flask and disposed of in a waste container. The wood chips were ignited with a Bunsen burner and placed in a glass container. After most of the chips' surface was burned, the fire was extinguished and the semi-charred wood chips were placed into a glass bottle and used for SPME extraction procedure.

### 2.3 Gas Chromatographic Analysis

Quantitative analysis for benzene and toluene was performed on Hewlett Packard Gas Chromatograph HP 6890 Series II Plus equipped with a flame ionization detector (FID). The column used was a HP-5 fused-silica capillary column, 30 m x 0.25 mm and 0.25  $\mu\text{m}$  film thickness. The GC temperature and condition were as follows: isothermal at 60  $^{\circ}\text{C}$ ; injection port temperature 250  $^{\circ}\text{C}$ ; detector temperature, 280  $^{\circ}\text{C}$ ; carrier gas (nitrogen) flow rate, 12.0 ml min<sup>-1</sup>.

### 2.4 Experimental Design

Statistical software package Design-Expert 6.0.6, an expert system for the design and analysis of experiments was purchased from Stat-Ease Inc. Minneapolis. A central composite design was applied with three experimental variables (factors), namely extraction

temperature, extraction time and desorption time. The coded levels and the values of the factors set in this statistical experiment are shown in Table 1.

The response variables selected were the gas chromatograph area count for

benzene, toluene, xylene and hexadecane. Two replications were performed at center point. The design matrix of the central composite design is shown in Table 2. The order of these experiments was randomized to remove any systematic error.

**Table 1.** Coded levels and values of the design factors.

Levels	Extraction temperature (°C)	Extraction Time (min)	Desorption time (s)
- $\alpha$	29	4	13
-1	34	8	40
0	40	14	80
1	46	20	120
+ $\alpha$	50	24	147

**Table 2.** Central composite design of the optimization experiment

Run Order	Extraction Time (min)	Extraction Temperature (°C)	Desorption time (s)
1	20.0	46.0	120.0
2	20.0	34.0	40.0
3	14.0	40.0	80.0
4	14.0	40.0	80.0
5	20.0	34.0	120.0
6	8.0	46.0	120.0
7	8.0	34.0	40.0
8	20.0	46.0	40.0
9	14.0	40.0	80.0
10	8.0	34.0	120.0
11	8.0	46.0	40.0
12	14.0	40.0	80.0
13	14.0	40.0	80.0
14	4.0	40.0	80.0
15	14.0	29.9	80.0
16	14.0	40.0	80.0
17	14.0	50.0	80.0
18	24.0	40.0	80.0
19	14.0	40.0	12.7
20	14.0	40.0	147.3

### 3. RESULTS AND DISCUSSION

#### 3.1 Optimization of SPME Operating Parameters

The results from the central composite design were fitted to a quadratic model. Analysis of variance (ANOVA) was performed on the design to determine which variables, if any, had a significant effect on the recovery of each compound. Results of the significance test for benzene and toluene are shown in Table 3.

{ **SHAPE \\* MERGEFORMAT** } It was found that for the recovery of benzene and toluene at the 95% confidence level (Prob > F is less than 0.05), three parameters (desorption time ( $D_t$ ), extraction time ( $E_t^2$ ), and extraction temperature ( $T^2$ )), were significant. For the recovery of xylene, two parameters (extraction time ( $E_t^2$ ),

and extraction temperature ( $T^2$ )), were significant. However, no variables were significant for the recovery of hexadecane.

A response surface methodology was used to find the optimum operating conditions for the SPME procedure. Since it was not possible to simultaneously plot the experimental response as a function of the significant variables, the effect of two variables on the extraction of benzene was considered separately (Figure 1).

Based on these analyses, the optimum operating conditions for SPME were: extraction time 14 minutes, extraction temperature 40 °C, and desorption time 80 seconds.

**Table 3.** Results of Significant Test (ANOVA) using Quadratic Model

Model	P value			
	Benzene	Toluene	Xylene	Hexadecane
	0.0342	0.0455	0.1159	0.4089
$E_t$	0.1430	0.2017	0.3006	0.9338
T	0.0846	0.0685	0.0604	0.3033
$D_t$	0.0349	0.0389	0.1675	0.0950
$E_t^2$	0.0076	0.0093	0.0229	0.2651
$T^2$	0.0137	0.0228	0.0431	0.7141
$D_t^2$	0.5988	0.7566	0.7892	0.0828
$E_tT$	0.7066	0.6216	0.6392	0.9831
$E_tD_t$	0.4253	0.5455	0.6734	0.8954
$TD_t$	0.6964	0.7454	0.6244	0.9378

### 3.2 Analysis of Accelerants in Fire Debris

The optimized extraction conditions were then applied in analyzing accelerant samples and fire debris samples. The chromatograms of fresh unleaded petrol and fire debris sample using unleaded petrol as accelerant are shown below (Figure 2). The two chromatograms showed a similar pattern for retention time from 2 to 7 minutes. Extra peaks were observed

from the fire debris sample due to other volatile compounds resulted from the burning process.

Diesel is a higher boiling point fraction composed of essentially C<sub>10</sub> to C<sub>25</sub> aliphatic hydrocarbons. Figure 3(a) showed a chromatogram of fresh diesel with eight main components that was observed in the chromatogram of the fire debris sample with diesel as the accelerant (Figure 3(b)).

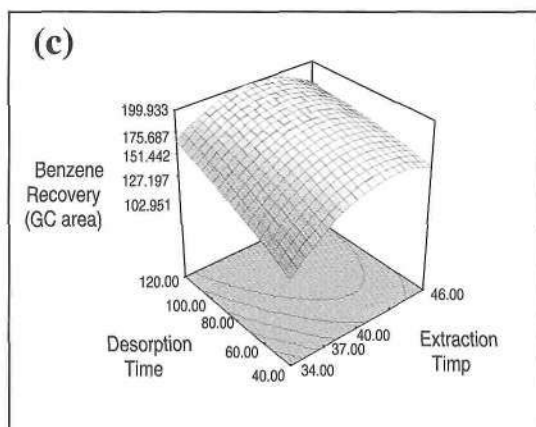
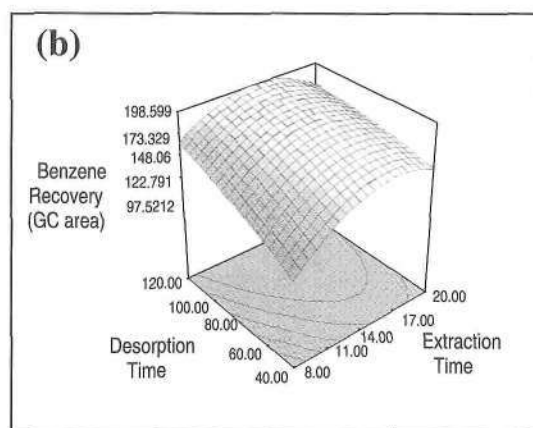
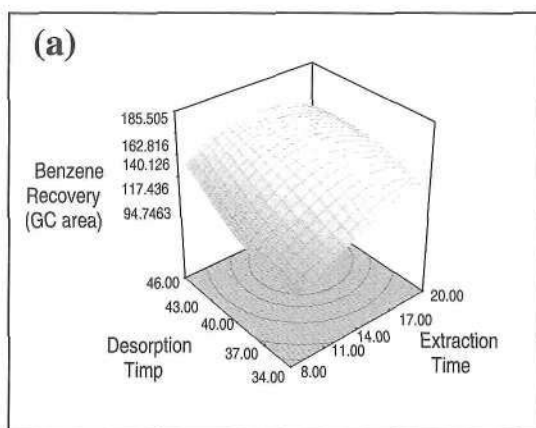
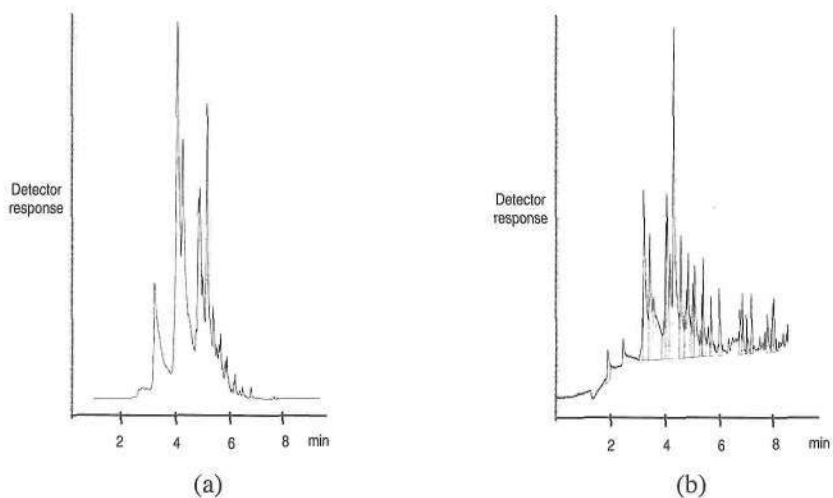
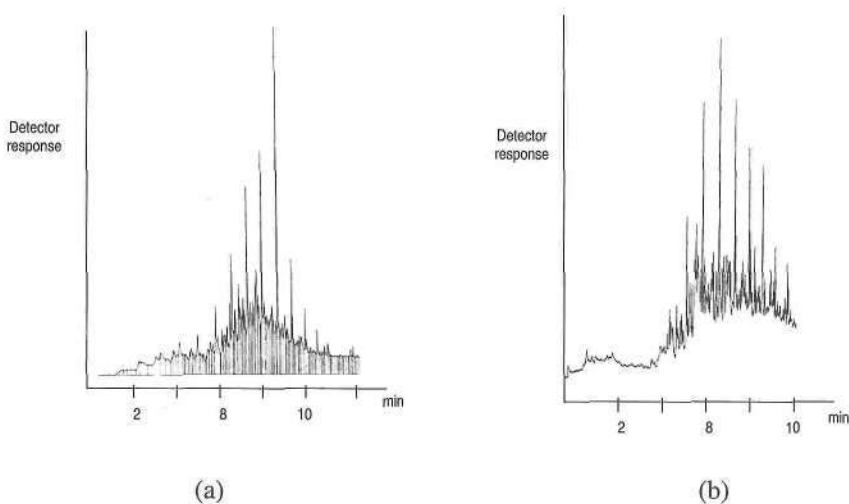


Figure 1: Response surface diagram: (a) the effect of extraction time and extraction temperature at desorption time of 80 s on the recovery of benzene, (b) the effect of desorption time and extraction time at extraction temperature of 40 °C on the recovery of benzene, and (c) the effect of desorption time and extraction temperature at extraction time of 14 minutes on the recovery of benzene



**Figure 2:** GC-FID chromatogram of (a) fresh unleaded petrol and (b) unleaded petrol recovered from fire debris sample.



**Figure 3:** GC-FID chromatogram of (a) fresh diesel and (b) diesel recovered from fire debris sample.



#### 4. CONCLUSION

In this study, the effect of three operating parameters of solid phase microextraction (SPME), such as extraction temperature, extraction time, and desorption time on the extraction of benzene, toluene, xylene, and hexadecane were evaluated using an experimental design based on central composite design. The optimized operating conditions for the extraction were identified using a response surface method. This study showed that SPME coupled to GC-FID is able to provide a fast, simple, and solvent-free method for the analysis of accelerants in fire debris.

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