

Simplex Optimization of Headspace-Enrichment Conditions of Residual Petroleum Distillates Used by Arsonists

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Simplex optimization analyzes varying factors simultaneously to obtain an optimal response. It is a powerful tool and represents the quickest way to obtain optimized conditions. Only a few structured laboratory exercises in methods development using simplex optimization have been described. These exercises include the optimization of fuel flow rate and burner position in atomic absorption spectroscopy (1) and the optimization of pH (concentration) in UV-visible spectroscopy (2). The first application is very practical; however, the optimization of experimental conditions for many instruments has already been done, and the optimal conditions are readily available from product manufacturers.

Simplex optimization is missing from most science curricula because it is time consuming and not practical for most teaching laboratory exercises. The problem occurs because a result must be obtained in order for new conditions to be determined. While this is not an issue in the real world, it is a problem for academic science labs that span three-hour blocks and need to cover a wide range of topics. Thus, science students typically encounter problems that focus only on physical relationships between two variables, consisting of a single independent and dependent variable.

We have developed a forensic exercise involving the analysis of accelerants typically used by arsonists. This lab is suited for either an individual or group project that spans multiple lab periods. This experiment is adaptable to teaching laboratories to give students practical experience using simplex optimization with the added benefit of using a real-world sample. In the apprehension and conviction of arsonists, forensic labs use a variety of sample-preparation and analytical methods. The identification of accelerants used by arsonists can be made because each accelerant has a "fingerprint", a characteristic pattern found in spectroscopic and chromatographic data, which is then compared to databases (3). An assortment of sample-preparation methods has been developed including distillation, solvent extraction, and headspace enrichment. The first two classical techniques are time consuming and labor intensive (4) and have recently been supplanted by the latter method.

Headspace-enrichment methods for sample preparation involve the adsorption of volatile compounds onto various materials. Generally, the debris is placed in a paint can, sealed and heated in an oven between 60 and 100 °C for 14–24 hours. The volatiles released from the debris are collected in the headspace of the can. In static methods, the volatiles are adsorbed onto an activated carbon strip, extracted with a solvent, and then analyzed. Since headspace enrichment is both time- and temperature-dependent, we analyzed different types

of accelerants using a simplex optimization procedure to determine the optimal conditions for sample preparation.

Experimental

A 10–20 μL sample of accelerant was spiked onto a Kimwipe, and this Kimwipe was placed in the bottom of an empty quart-size paint can with a nonstick coating. An activated charcoal strip (Albrayco Laboratories, Inc., Cromwell, CT) was speared onto a bent paperclip, the paper clip was attached to a piece of string, the string was suspended across the top of the can, and the can was sealed. Each paint can was heated in a drying oven at different temperatures (from 40 to 110 °C in 5 °C increments) for varying times (0.5 h increments), then they were removed and cooled for 10 min. The carbon strip was soaked in 100 μL of carbon disulfide for 20 min. A 3- μL aliquot of the extract was injected into a HP 5890 gas chromatograph fitted with a 30-m cross-linked methyl siloxane column and a flame ionization detector.

Data Analysis and Simplex-Optimization Method

Chromatograms were obtained and compared between the neat and headspace-enriched accelerants. Chromatographic peaks selected for comparison between the neat and extracted samples were chosen based on their intensity and contribution to the distinctive peak pattern for each accelerant. The differences in selected normalized peak heights between the neat and headspace-enriched samples were calculated and a residual was determined (Supplemental Materials^W). Based on the residual determined from multiple runs of a standard, the RNS (ratio of noise-to-signal) was calculated to be less than 5%, and therefore appropriate for simplex optimization (5).

The optimization procedure involved creating a simplex or geometric figure defined by $n + 1$ points, where n is the number of variables being optimized. In this application, a three-point simplex was needed to simultaneously optimize two independent variables, headspace enrichment time and temperature. Then, the points or trials were assigned as the best response, B , the worst response, W , and the next-to-worst response, N . The trial with the smallest residual was assigned as the best response. The next trial was determined by a set of rules previously described in this *Journal* (see the Supplemental Material for the specific rules; refs 2, 6, 7). Initially, the worst response is reflected through the center of a line that connects the best and next-to-worst response. This new point, or response, R , was used to determine the next set of

conditions. Subsequent trials involved additional reflections, R' , expansions, E , or contractions, C_W —contraction towards worst response or C_R —contraction towards a response, until satisfactory optimal conditions were obtained.

Hazards

Carbon disulfide is toxic and needs to be handled in a vent hood. Since small volumes of solvent were used, no significant waste was generated. Excess solvent was allowed to evaporate in a hood.

Results and Discussion

Accelerants have been divided into five classes as illustrated in Table 1 (8), and examples of chromatograms for each of the different classes of petroleum distillates are shown Figure 1. The first four classes are petroleum distillates, while class zero consists of nonpetroleum products. The time and temperature used in headspace-enrichment methods is crucial in sample preparation since molecular weight and structure primarily distinguish the petroleum distillate classes. It has been demonstrated (9) that higher temperatures or longer

enrichment times selectively adsorb molecules with higher boiling points. Likewise, temperatures below 60 °C are not adequate to volatilize heavy petroleum products.

The optimal conditions for headspace enrichment were determined by simplex optimization for a sample from each petroleum distillate class. Appropriate blanks were analyzed and chromatograms only contained peaks associated with the solvent. The optimal condition for the enrichment of accelerants was determined by minimizing the residual until the RNS was no greater than 5%. Additional trials were also examined for each sample to determine how the conditions influenced the shape of the chromatograms.

An example of the simplex optimization for gasoline is shown in Figure 2. The original simplex was defined by one hour at 50 °C, two hours at 75 °C, and four hours at 65 °C. Rules for simplex optimization, as discussed previously (6), indicate an impossible reflection for the fourth trial. Thus, a large response or residual is input into the simplex for this trial, and a C_W contraction is then recommended (Figure 2A). The inset of this figure illustrates the magnitude of the residual of each actual trial. The subsequent reflections and residuals that were used to obtain the optimal conditions for gasoline are shown in Figure 2B.

Table 1. Accelerant Classification System

Class	Description	Examples
0	Nonpetroleum products	Alcohols
1	Light petroleum distillates	Petroleum ethers, lighter fluid
2	Gasolines	Gasoline, camp stove fuels
3	Medium petroleum distillates	Paint thinner, charcoal lighter fluid
4	Kerosene and heavy petroleum distillates	Jet fuel, insect spray, diesel fuel

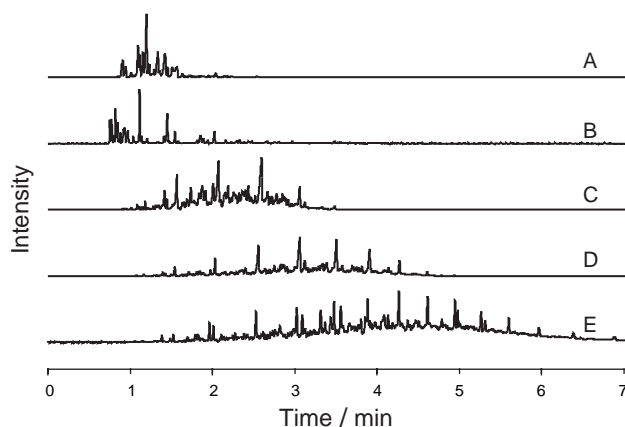


Figure 1. Chromatograms of (A) lighter fluid, (B) gasoline, (C) paint thinner, (D) kerosene, and (E) diesel fuel.

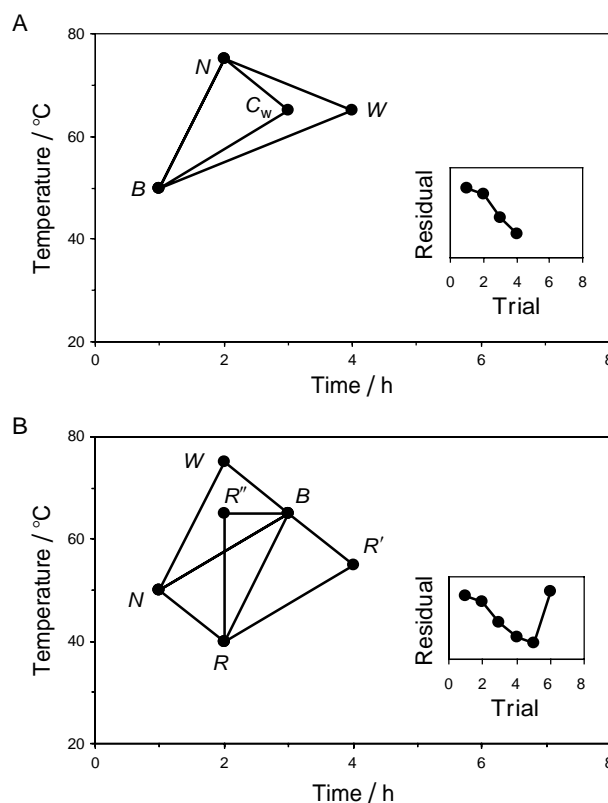


Figure 2. (A) Simplex and (B) the new simplex utilized to optimize solid-phase enrichment conditions for gasoline. The best, next-to-worst, and worst residual for the simplex are noted as B , N , and W , respectively. The calculated contraction for the next trial is C_W . The three resulting reflections are noted as R , R' and R'' . The inset illustrates the residuals obtained for successive trials.

Chromatograms of kerosene that were obtained under different headspace-enrichment conditions are illustrated in Figure 3. It can be seen from this figure that at long enrichment times (18 h) and high enrichment temperatures (90 °C), the chromatogram over represents the fraction of components with longer retention times and underestimates the fraction of components with short retention times. To further illustrate this phenomenon, the differences between normalized peaks of neat and headspace-enriched diesel are shown in Figure 4 (other examples are in Supplemental Materials^{III}). At relatively short times and low enrichment temperatures, the diesel fuel components with short retention times were over represented, and the reverse was true for components with long retention times.

The optimal conditions for sample enrichment for the different accelerants, and our original simplex conditions are all illustrated in Figure 5. Since accelerant classes are essentially distinguished by molecular weight, it would be expected that the time and temperature for optimal enrichment would increase with accelerant classification. For the most part, this behavior was observed. The optimal conditions for lighter fluid, a class 1 accelerant, was between a class 2 and 3 accelerant, and it can be seen from the chromatogram in Figure 1 that lighter fluid contained components that had retention times that were between those of gasoline and paint thinner.

An interesting finding of this study is that most forensic labs following ASTM guidelines are using less-than-optimal enrichment conditions, and then these data are compared with library standards. Based on earlier studies (9), it has been recommended that samples suspected of containing high molecular weight fuels be enriched overnight or longer, and this is common practice in forensic labs (10). Our studies indicate that these samples can be successfully extracted in less

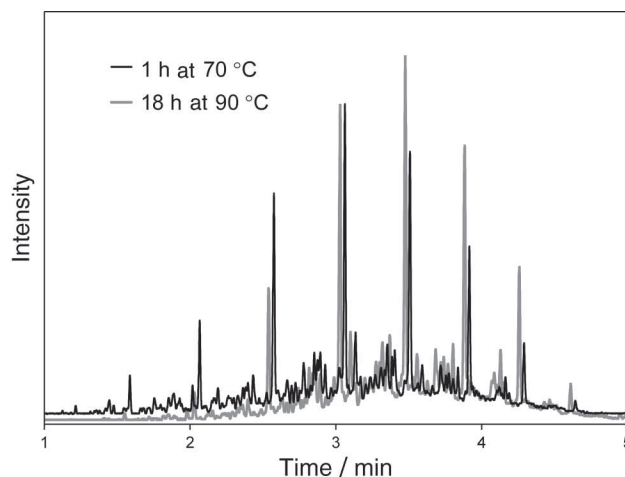


Figure 3. Chromatograms of kerosene enriched for 1 h at 70 °C (black line) and 18 h at 90 °C (gray line). Chromatogram retention times were offset for clarity.

than 5 h. Since enrichment conditions alter the distribution of accelerant components, it will be crucial that samples be extracted under optimized conditions to compare their chromatograms with those found in databases.

Conclusion

An analytical laboratory exercise is described to introduce undergraduates to simplex optimization. In addition to the time it takes to heat the sample, it takes about 40 min to

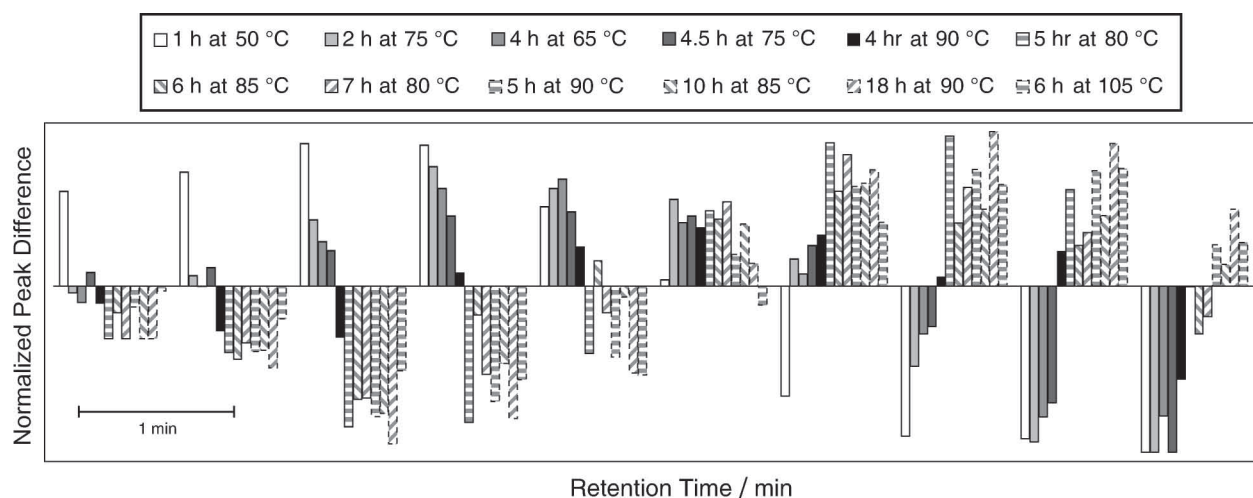


Figure 4. Difference in normalized peak heights between neat and headspace-enriched diesel fuel. Times and temperatures that are below, at, and above optimal conditions are represented by white and shades of gray, black, and striped patterns, respectively.

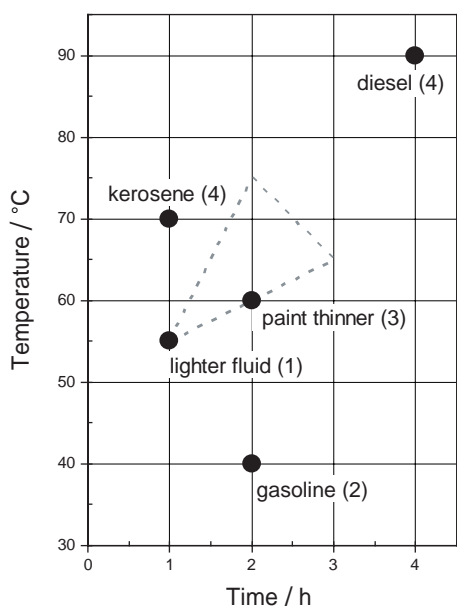


Figure 5. Recommended headspace-enrichment conditions for petroleum distillate accelerant classes (in parentheses). The gray dashed line represents the original simplex used to determine optimal enrichment conditions.

prepare the sample, cool it, and run a chromatogram. The heating times could be shortened to allow for this experiment to be completed in a 3–4 hour laboratory session. Additional trials would be carried out in a second laboratory session. An alternative rapid approach would be to use simplex opti-

mization in conjunction with solid-phase micro extraction (SPME). This technique has enrichment times of less than 30 min for accelerants (3). A disadvantage to SPME is that the syringes can be broken easily if mishandled.

Acknowledgment

The Minnesota Chromatography Forum is gratefully acknowledged for financial support to M. Warnke.

^wSupplemental Material

A student handout, including pre- and postlab questions, notes for the instructor, and simplex rules are available in this issue of *JCE Online*.

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