TECHNICAL NOTE

Laurel V. Waters,[1] *B.S. and Lee A. Palmer,*[1] *B.S.*

Multiple Analysis of Fire Debris Samples Using Passive Headspace Concentration

ABSTRACT: Recent advances in the field of fire debris analysis have resulted in the development of the passive headspace concentration method for the separation of flammable and combustible liquid residues from debris. Not only is this method applicable to most sample matrices, but because it is essentially nondestructive, multiple passive separations can be performed on a given sample yielding the same results.

KEYWORDS: forensic science, fire debris analysis, passive headspace concentration, active headspace concentration, charcoal strip, extraction, flammable and combustible liquid residues

One of the most commonly used and efficient methods for the separation of flammable and combustible liquids from debris samples has been dynamic headspace concentration, better known as the purge and trap, or the charcoal-tube method [1,10]. Several years ago, Twibell and Home [2] developed a new method, passive headspace, which used the Curie point pyrolysis system. This technique was later modified by Twibell [3] and Andrasko [4]. In 1982 Juhala [5], also using a charcoal-coated wire inserted into the sample headspace, used a solvent to elute trapped accelerant residues, which allowed the extract to be reanalyzed if necessary. Reeve [6] later modified this technique by using cyrogenic focusing and Tranthim-Fryer [7] reported using n-pentane as the extraction solvent. More recently, Dietz [8] reported using the C-bag and charcoal strips, both of which were suspended within the headspace of the debris sample and desorbed using carbon disulfide.

Because dynamic headspace is an active process, it is reasonable to assume that in certain cases, any accelerant residue remaining in the debris sample may be significantly reduced making successive separations difficult at best. This may be especially true for samples containing very low levels of accelerants recovered after the initial separation. Unless the sample has a distinguishable odor or the extract is available and preserved (by the addition of charcoal or some other adsorbent) another analyst will almost certainly be unable to reproduce the original results several months or years down the road. In this paper, we will explore the nondestructive nature of passive headspace separation, utilizing the charcoal strip, and its significance in the field of fire debris analysis.

Materials and Methods

Separation Technique

The adsorption material used in the separation was a charcoal impregnated binder manufactured by Pro-Tek Systems, Inc. (Portland, CT). One third of a ½″ × 2¾″ strip attached to a safety pin was suspended inside the debris container and heated to 80°C for a period of 16 to 18 h. Additionally, 1 μL of 3-phenyltoluene was added to the sample as an internal standard. The charcoal strip was removed from the sample and transferred to a 10 × 75 mm borosilicate glass culture tube and eluted with approximately 0.5 mL of carbon disulfide (E. M. Science, Gibbstown, NJ). A layer of deionized water was added to prevent the evaporation of the carbon disulfide [9].

Gas Chromatography

Gas chromatographic (GC) analyses were performed using a Perkin-Elmer Sigma 2B gas chromatograph fitted with a flame ionization detector. A 30 m fused silica SPB-1 capillary column with a 0.32 mm ID and a 0.25 μm film thickness (Supelco, Inc., Bellefonte, PA) was used to perform the separations. The helium carrier gas flow rate was 2 mL/min with a 30:1 split. The oven was set at an initial temperature of 60°C with a 3 min hold time, then programmed at a rate of 30°C per min. to a final temperature of 300°C. The injector and detector temperatures were set at 250°C and 290°C, respectively. All data was processed using an Apple IIe data system with Appligration Software (Millipore Corp., Bedford, MD).

Test Samples

A total of 12 samples were selected for the study. Each sample was from an actual case that was previously separated by passive headspace concentration and determined to be positive for the presence of a flammable or combustible liquid using the identification and classification system as described in ASTM Method E 1387-90 [11]. There were no samples containing mixtures selected for the study. The concentrations of flammable or combustible liquid in the sample extracts were on the same order of magnitude as the standards used for comparison, approximately 1%.

The samples were subdivided into four groups of four samples each. Each group contained two debris samples positive for gasoline, one debris sample positive for a medium petroleum distillate, and one debris sample positive for a heavy petroleum distillate. There was not a sufficient number of samples from actual cases that contained a light petroleum distillate and fit into the time frame to be included in the study. Ideally, we would have preferred for each test group to be composed of six samples, one from each of the classification groups. In an attempt to compensate for the lack of light petroleum distillate (LPDs) two gasoline samples, one less weathered than the other, were selected for each group.

Results

Group A

The samples in Group A were each separated a total of four times: when originally submitted for analysis and at 30, 90, and 180 day intervals from the original date of separation. The concentration of the accelerant residue detected in some of the samples was slightly diminished with each successive separation. No difficulty was encountered however, in making the same positive identification after the successive separations. The chromatograms in Figs. 1 through 4 illustrate all four of the separations from the samples in Group A.
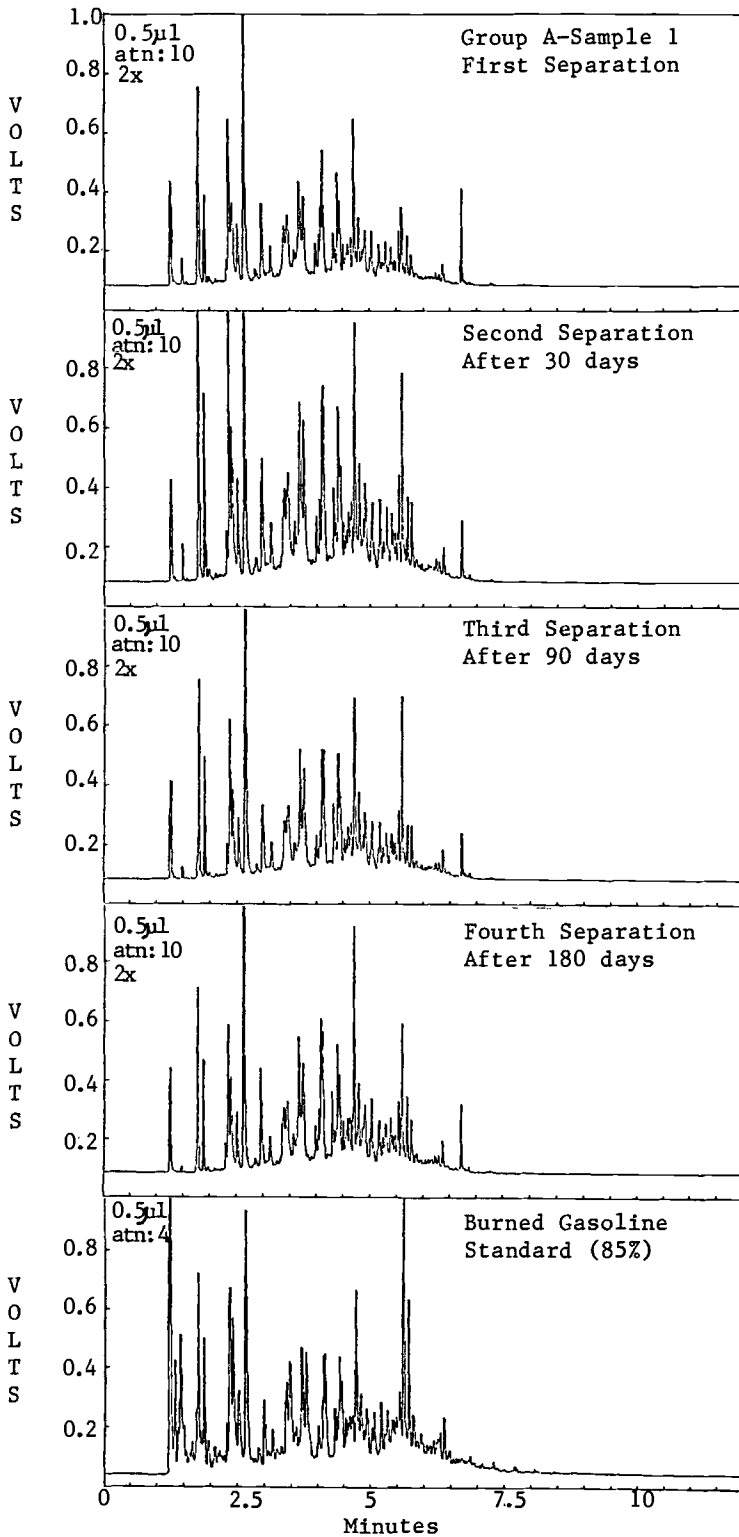
FIG. 1—*Chromatograms of each of four successive separations of Sample 1, Group A, and an 85% burned gasoline standard.*
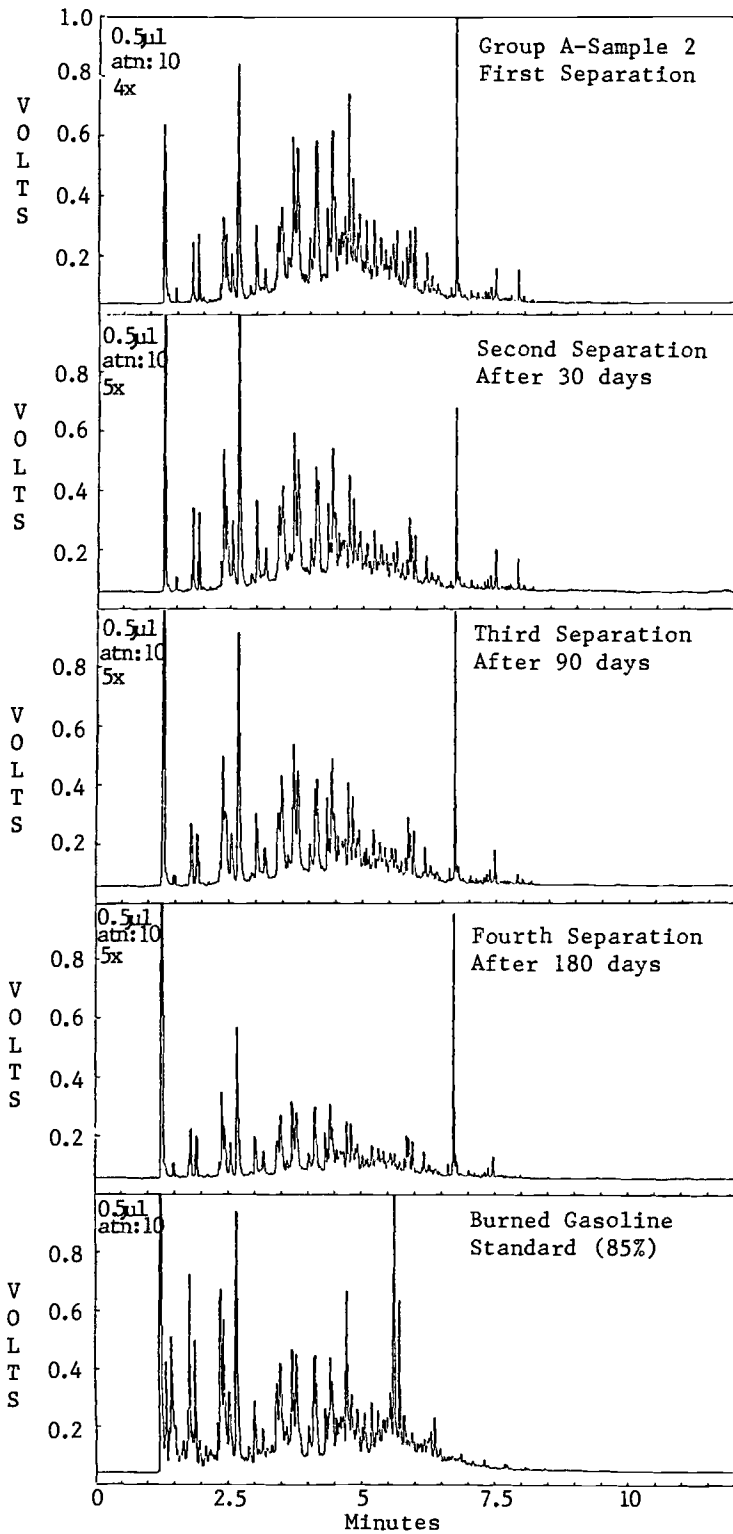
FIG. 2—Chromatograms of each of four successive separations of Sample 2, Group A, and an 85% burned gasoline standard.
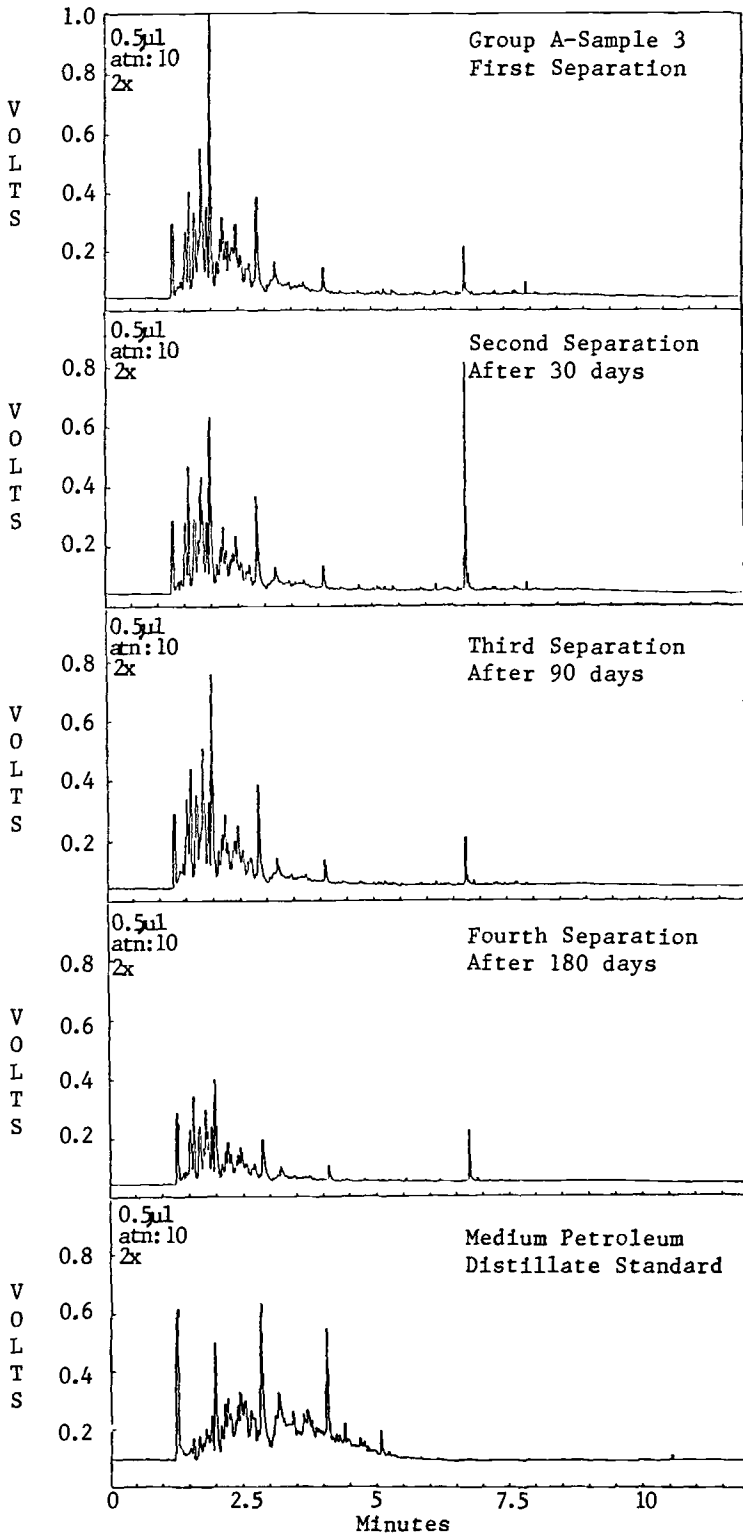
FIG. 3—*Chromatograms of each of four successive separations of Sample 3, Group A, and a medium petroleum distillate standard.*
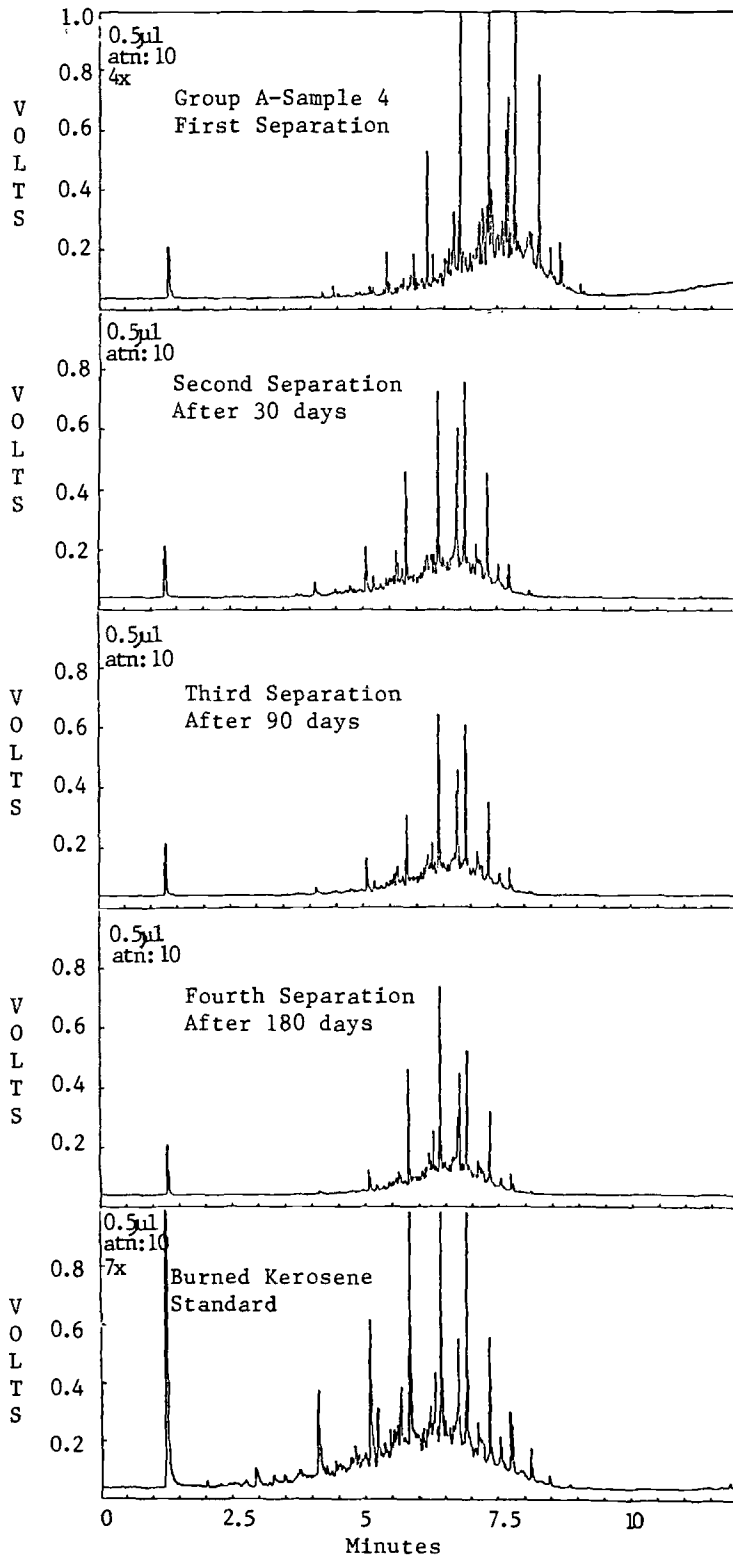
FIG. 4—*Chromatograms of each of four successive separations of Sample 4, Group A, and a heavy petroleum distillate standard.*

Group B

The samples in Group B were separated at time intervals of 90 and 180 days from the original separation date, making a total of three separations. Again, although the amount of volatiles recovered from each sample was slightly reduced after each separation, the same positive results were obtained after each successive separation (Figs. 5–8). The most significant changes occurred in sample 1, which contained a light gasoline residue.
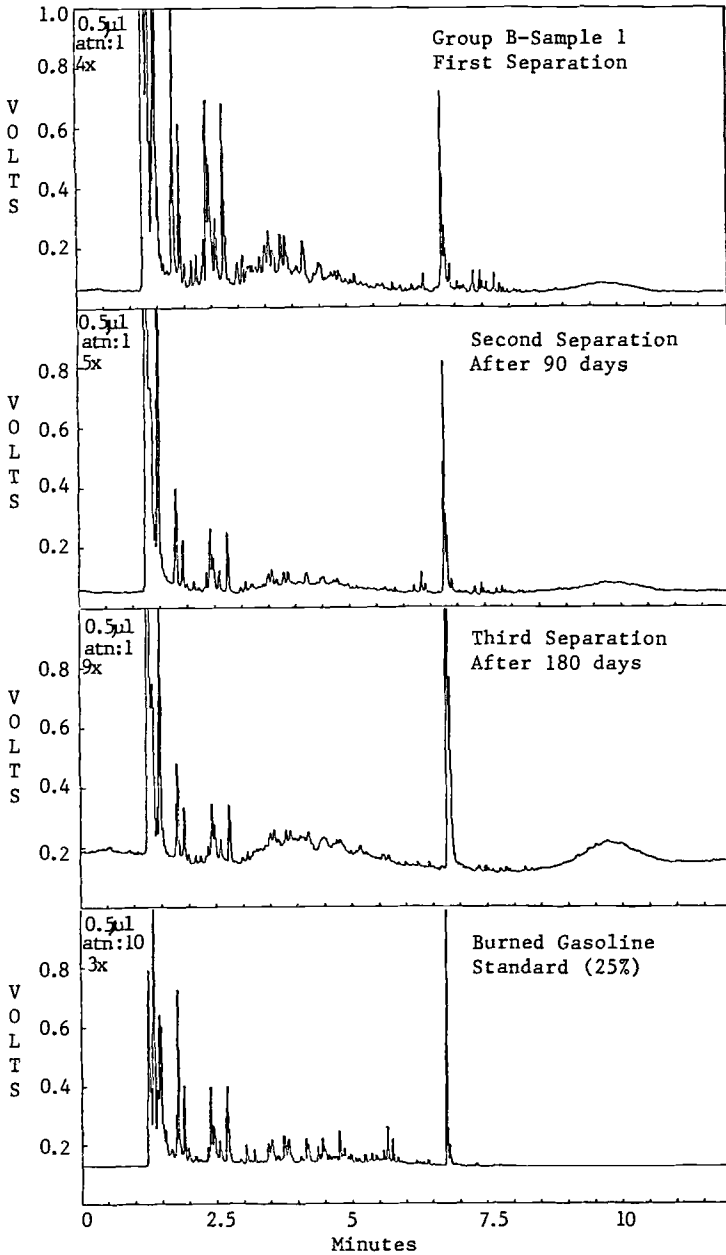
FIG. 5—*Chromatograms of each of three successive separations of Sample 1, Group B, and a 25% burned gasoline standard.*
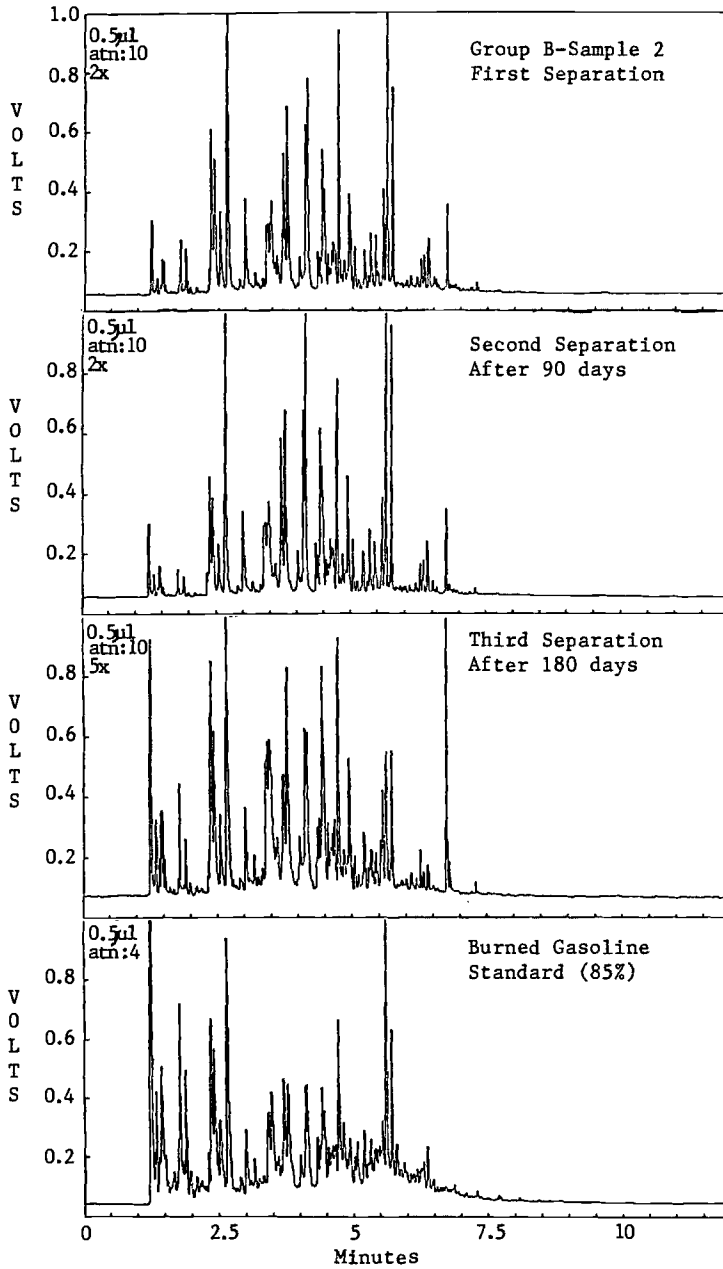
FIG. 6—*Chromatograms of each of three successive separations of Sample 2, Group B, and an 85% burned gasoline standard.*
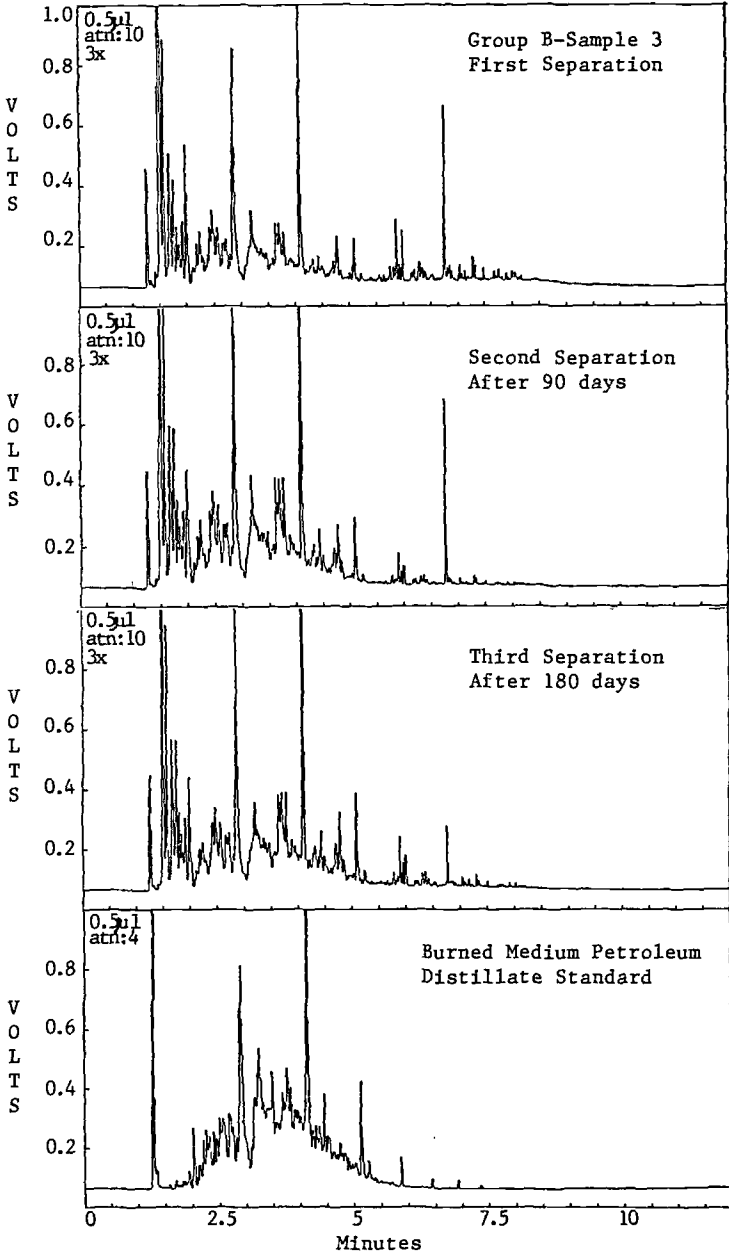
FIG. 7—*Chromatograms of each of three successive separations of Sample 3, Group B, and a medium petroleum distillate standard.*

Group C

The samples in Group C were separated 180 and 365 days after the initial separation date, making a total of three separations (Figs. 9–12). The volatile components were again easily identified and the same positive identification within each classification group
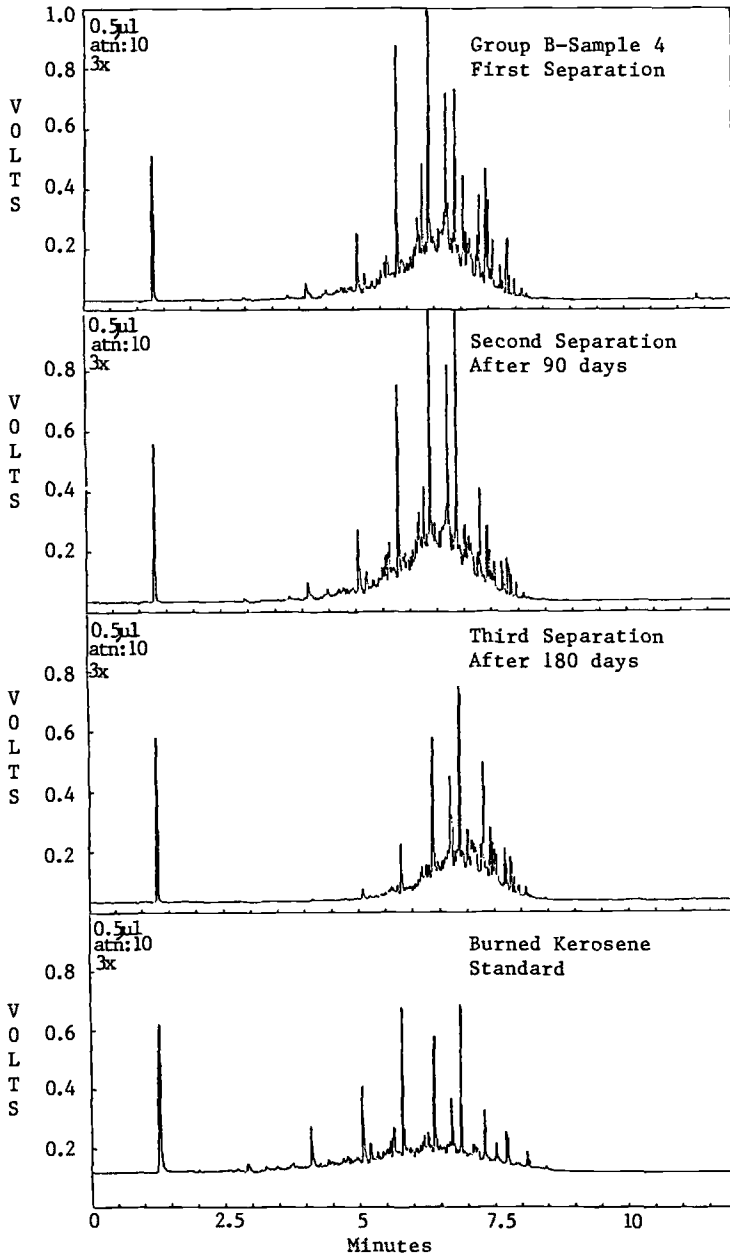

FIG. 8—*Chromatograms of each of three successive separations of Sample 4, Group B, and heavy petroleum distillate standard.*
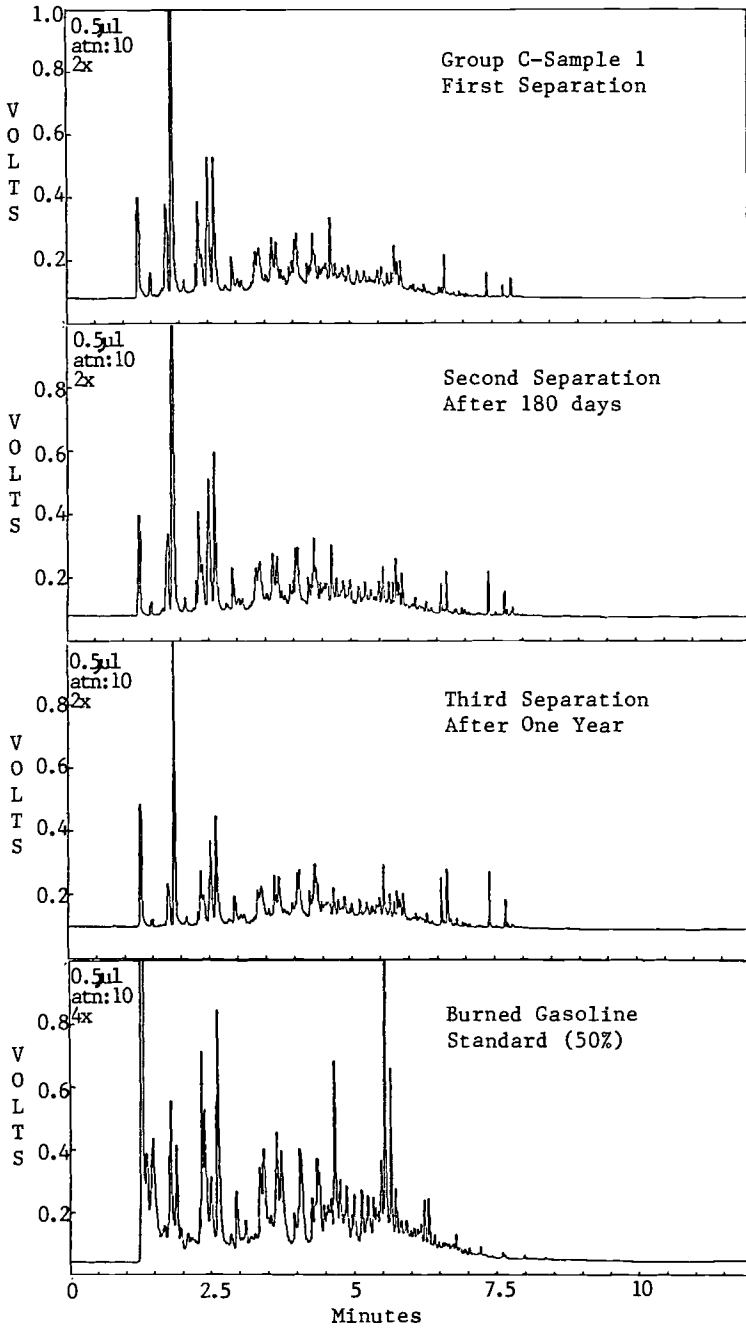
FIG. 9—*Chromatograms of each of three successive separations of Sample 1, Group C, and a 50% burned gasoline standard.*

was achieved after the repeated separations. One sample, classified a heavy petroleum distillate (HPD), further identified as kerosene, exhibited a significant change in the concentration and the distribution of the aliphatic compounds. As seen in the chromatograms in Fig. 11, the range of the n-alkanes after the first separation was from C_{11} to C_{18}, well within the normal range for kerosene. After the third separation (one year
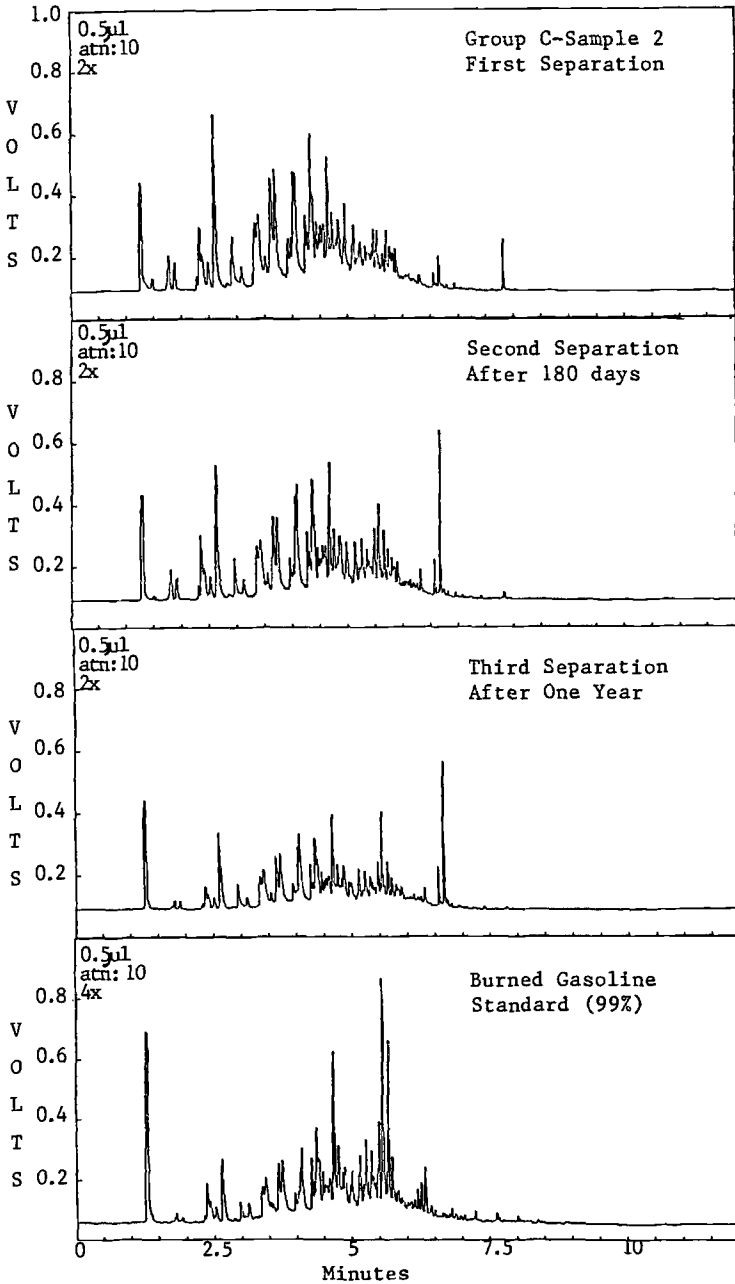

FIG. 10—*Chromatograms of each of three successive separations of Sample 2, Group C, and a 99% burned gasoline standard.*

later), the range shifted to C_{13} to C_{20}. The pristane and phytane peaks were more easily observed after the third separation.

Group D

The samples in Group D were separated 365 days after the initial separation date (Figs. 13–16). As with the previous three groups, there was some decrease in the re-
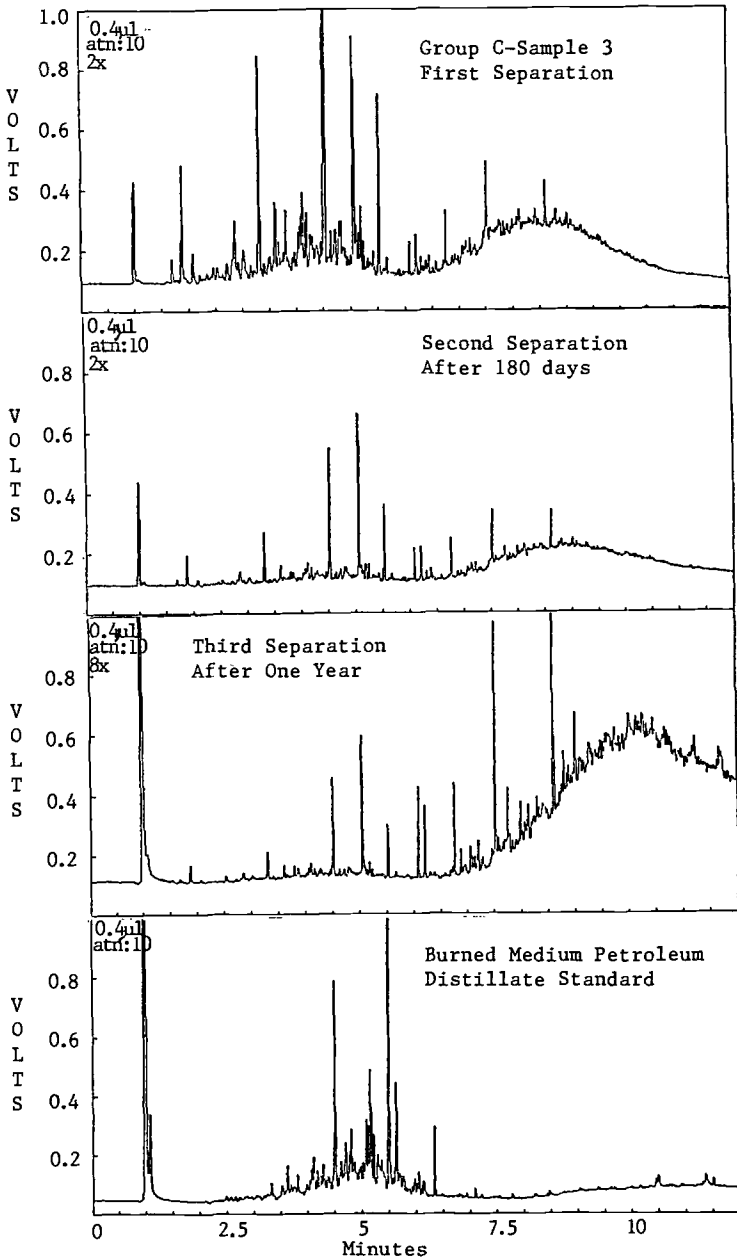

FIG. 11—*Chromatograms of each of three successive separations of Sample 3, Group C, and a medium petroleum distillate standard.*
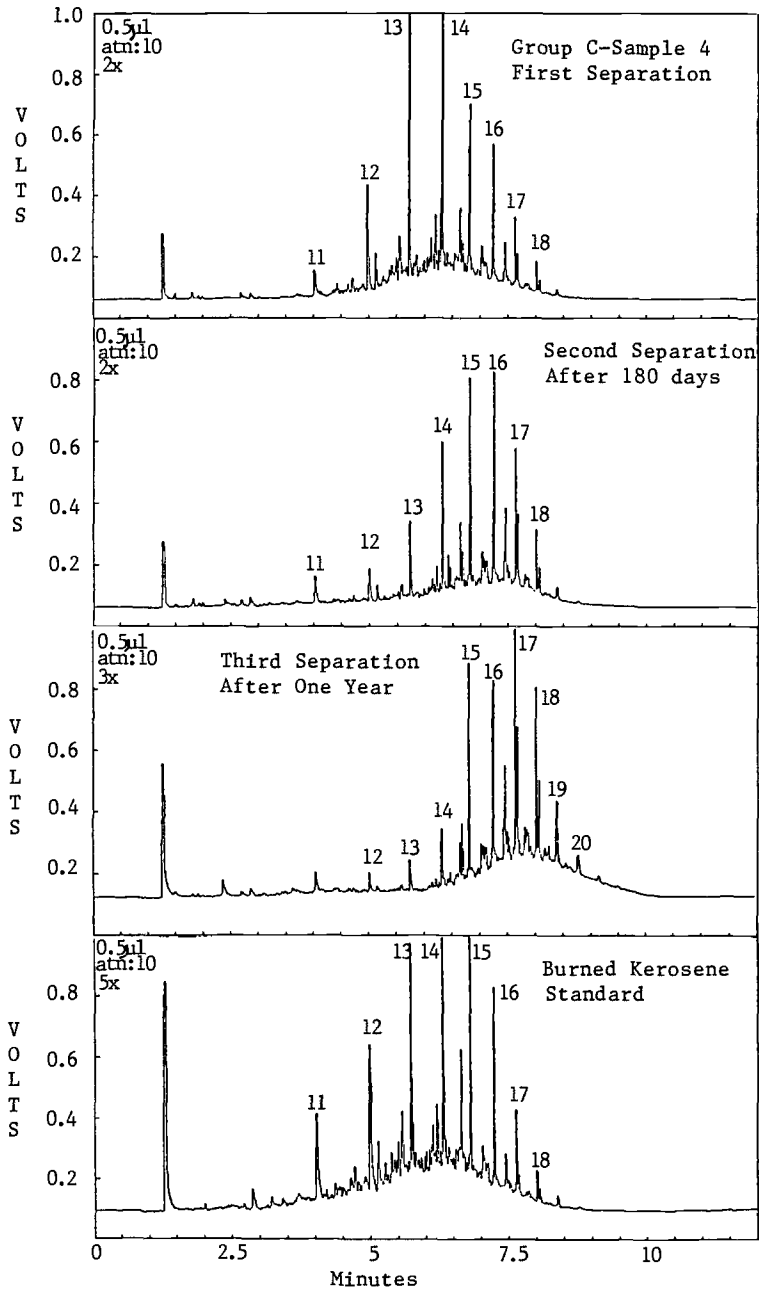
FIG. 12—*Chromatograms of each of three successive separations of Sample 4, Group C, and a heavy petroleum distillate standard.*
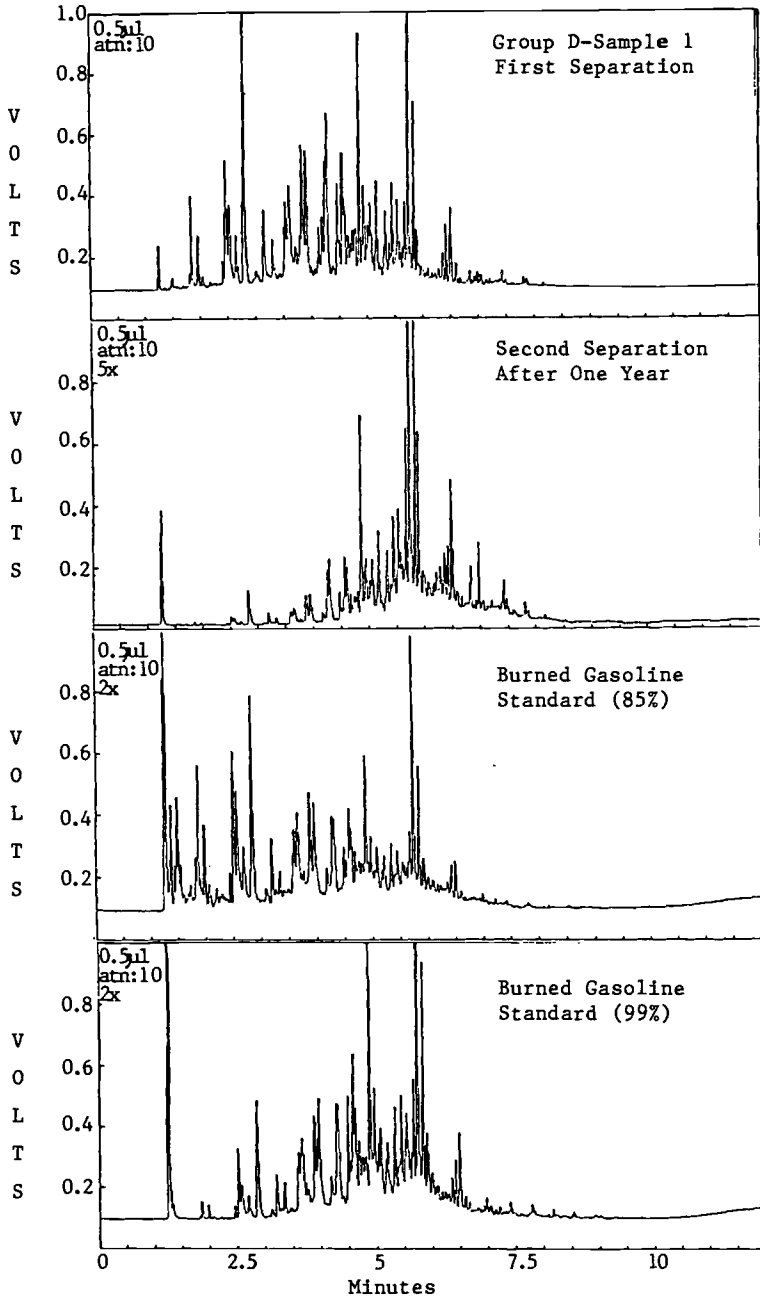
FIG. 13—*Chromatograms of each of two successive separations of Sample 1, Group D, an 85% burned gasoline standard and a 99% burned gasoline standard.*
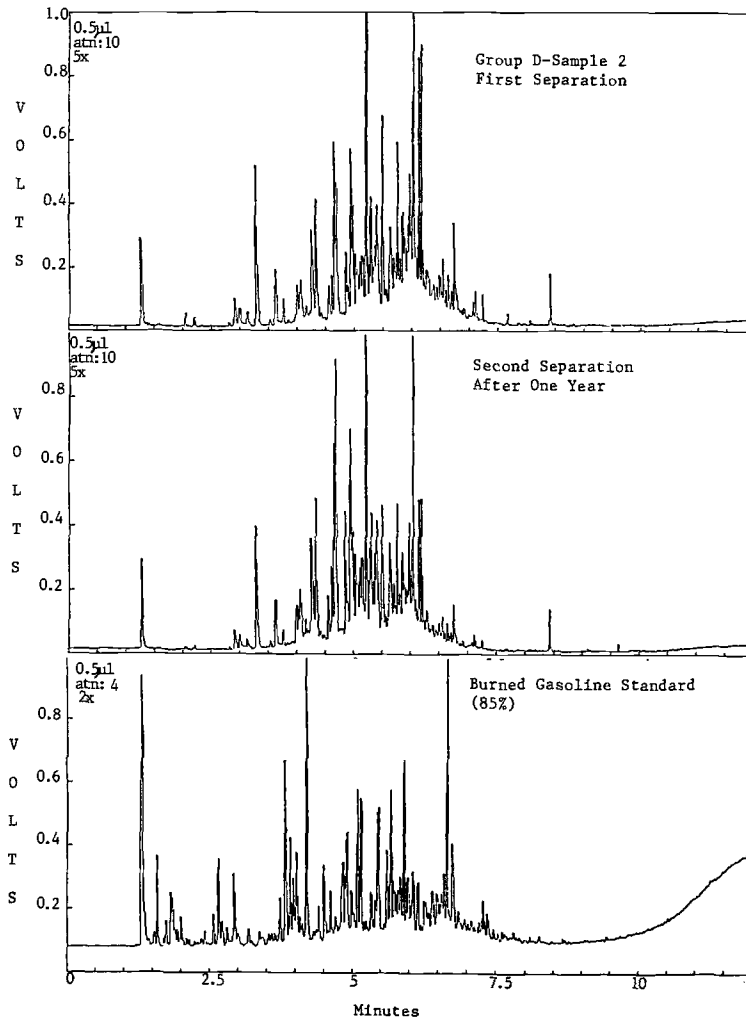
FIG. 14—*Chromatograms of two successive separations of Sample 2, Group D, and an 85% burned gasoline standard.*

coverable volatile components after the second separation. The chromatograms from a sample containing gasoline (Fig. 13) indicate a significant change in the volatile components recovered one year after the original analysis date. The original separation and analysis revealed a mixture of components corresponding to a standard of 85% evaporated gasoline. One year later the residue recovered from the sample was more in the range of approximately 99% evaporated gasoline.

Discussion

The results of the analysis from the four test groups show that multiple separations by passive headspace can be performed without jeopardizing the recovery and identification of the volatile residues. Although some reduction in the concentration of the volatile
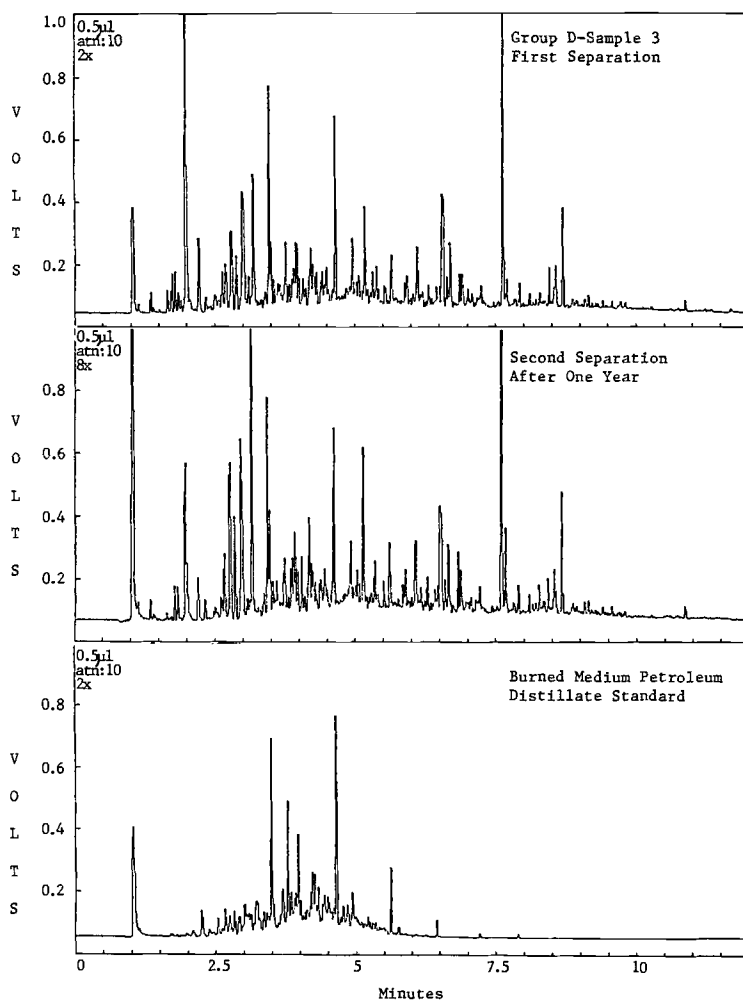
FIG. 15—*Chromatograms of each of two successive separations of Sample 3, Group D, and a medium petroleum distillate standard.*

components recovered from a few of the samples did occur, identification was still easily accomplished using the ASTM classification system. The only significant changes induced by the separation process seem to occur in light residues such as slightly weathered gasoline. LPDs may change similarly.

Since using this technique, we have not only discovered the viability of multiple separations, but additional advantages as well. The possibility of contamination when using passive headspace is dramatically reduced. Active headspace concentration requires either the use of a vacuum system or forced air or nitrogen, both of which, if not used cautiously, can introduce contamination into the sample. With the closed system of passive headspace concentration this problem is eliminated.

Additionally, sample preparation time is greatly reduced, in that the separation process requires little set up and monitoring, and the separation can almost always be done in the original sample container.
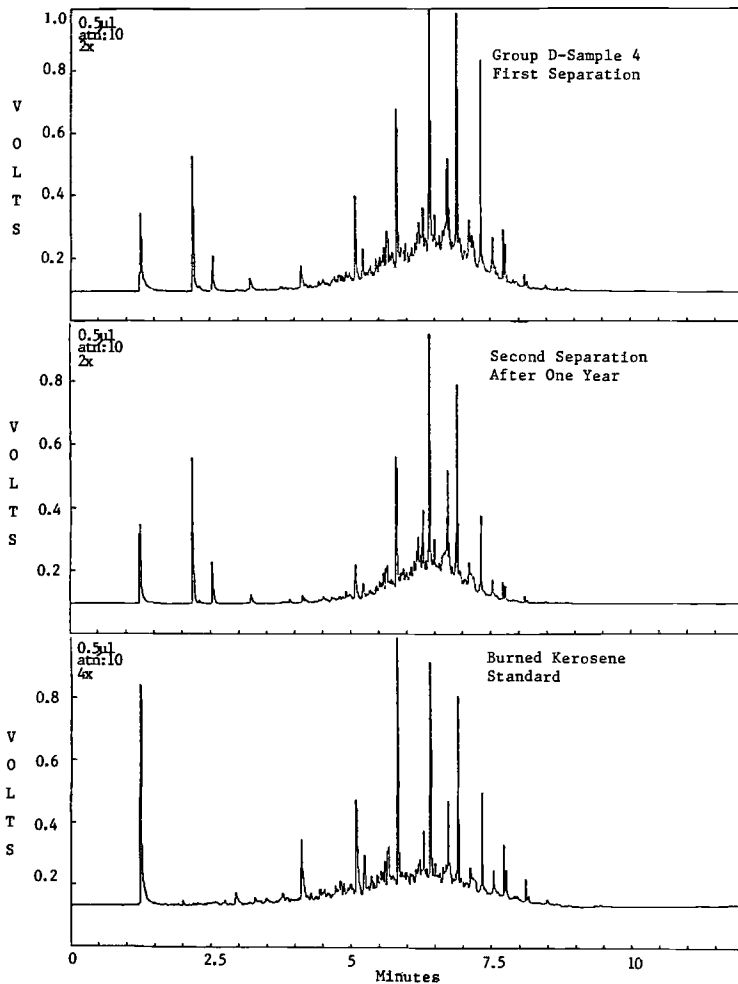
FIG. 16—*Chromatograms of each of two successive separations of Sample 4, Group D, and a heavy petroleum distillate standard.*

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Address requests for reprints or additional information to
Laurel V. Waters
Analytical Forensic Associates, Inc.
3250 Peachtree Corners Circle
Suite I
Norcross, GA 30092