# Fast Gas Chromatography of Various Sample Types Using Fast Oven Temperature Programming

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## Abstract

**Applications of fast gas chromatography (GC) using rapid column oven temperature programming are described for a variety of samples including standard solutions of hydrocarbons and polycyclic aromatic hydrocarbons and more complex samples including perfumed mineral oil and food products. Results for the standard solutions using fast temperature programming GC are compared with those using conventional GC and fast GC on a conventional instrument. The more complex samples are analyzed using fast oven temperature programming, demonstrating precision in the chromatographic data as well as the feasibility of quantitation when doing a fast GC analysis. Many applications can be run much faster than with published conventional GC methods without significant loss in resolution.**

## Introduction

Fast GC is not a new technique, but its popularity is growing. When Golay (1) introduced his open-tubular column in Amsterdam in 1958, people realized that capillary columns would be much faster because of their lower flow impedance, higher linear gas velocities, and longer column lengths. Soon after the introduction of the open tubular columns, Desty (2) realized that a significant reduction in analysis time was possible by reducing the internal diameter of the column. In the years since, Cramers and his group at Eindhoven Technical University have published several papers on fast GC (3–6). However, in the early development of GC, fast GC for routine analysis was not practical because of the limitations of the GC injection ports, GC detectors, and columns. Over the past 40 years, there have been significant improvements made to all of these components. These improvements, as well as computer technology, have opened the way for introducing fast GC for routine analysis. Currently, there is a strong emphasis to use fast GC for routine analysis because of the increased sample throughput and the possibility for increased precision due to the capability of running duplicate samples and more standards in the same time period.

The important parameters for fast GC are shorter column lengths, smaller internal diameters, thinner liquid phase films, higher pressures, faster flow rates, and faster column oven temperature programming. Two of the key factors in faster GC are shorter columns and faster oven temperature programming rates. Both result in some loss in resolution, but this is partially offset by the use of thinner films and smaller internal diameters.

Recently, new instrumentation has been introduced that is capable of fast column oven temperature programming (up to 1200°C/min)(7). This is an important capability for fast GC, especially when the sample of interest contains analytes with a wide range of boiling points. For these fast programming rates, the column is wrapped inside metal tubing that is resistively heated (7). van Lieshout et al. (8) discussed this methodology using a PONA (paraffins, olefins, naphthalenes, and aromatics) sample and found that it could significantly reduce the analysis time.

One argument against fast GC is that long sample preparation times negate any savings brought about in the analysis itself. In some cases this may be true; however, there are several newer sample preparation methods that can be used to significantly shorten extraction times in comparison with classical liquid–liquid or Soxhlet extractions. These faster methods include microwave assisted extraction (MAE), solid-phase extraction (SPE), solid-phase microextraction (SPME), and supercritical fluid extraction (SFE). MAE is used in this work as a fast sample preparation technique for various food products. In the literature, the analysis of 2,6-di-(*tert*-butyl)-4-methylphenol (commonly know as BHT) in breakfast cereals and chewing gums was performed using a 16-h solvent extraction followed by a 60-min GC analysis (9) and short-path thermal desorption sample preparation followed by a 35-min GC analysis (10). In this work, MAE and a 3-min GC analysis time were used.

Another issue that is often raised is the reproducibility of peak areas and retention times in fast GC. This issue is also addressed in this paper using a perfumed mineral oil sample; the peak area and the peak retention time precision results are comparable with conventional GC.

## Experimental

### Instrumentation

The GCs included a 240 V HP model 6890 GC (Hewlett-Packard, Wilmington, DE), an HP model 5890 GC equipped with an EZFlash (Thermedics Detection, Chelmsford, MA), and a Perkin Elmer Autosystem XL (Perkin Elmer, Norwalk, CT). All GCs were equipped with flame ionization detectors (FID). The columns were HP-5 (Hewlett-Packard), HP-1 (Hewlett-Packard), or PE-1 (Perkin Elmer) stationary phases of various dimensions (detailed in the individual analyses). The autosampler was a Hewlett-Packard HP 7673 or a Perkin Elmer Autosystem XL autosampler. Various column oven temperature programs were used depending on the sample. The data collection was accomplished with either an HP ChemStation or a PE Turbochrom system. The MES model 1000 (CEM Corporation, Matthews, NC) microwave extractor was used to extract the food products.

### Reagents

The hydrocarbon sample was a 100-ppm solution of nonane through heptadecane in hexane prepared from standards available in our laboratory. PAHs were obtained from Hewlett-Packard (part number 8500-6035). The food samples were purchased from a local supermarket. The gel candles were purchased from a local store.

### Sample Preparation

The microwave extraction used a hexane–isopropanol (90:10) solvent mixture and 100% power of 950 watts. The extraction times were 1 min for 0.1 g of chewing gum in 5 mL solvent, 5 min for 1 g of cereal in 5 mL solvent, and 5 min for 1 g of a granola bar in 5 mL solvent. Prior to extraction, the chewing gum was cut into small pieces and the cereal was crushed in a food blender. Following the microwave extraction, the extracts were filtered, adjusted to volume, and analyzed.

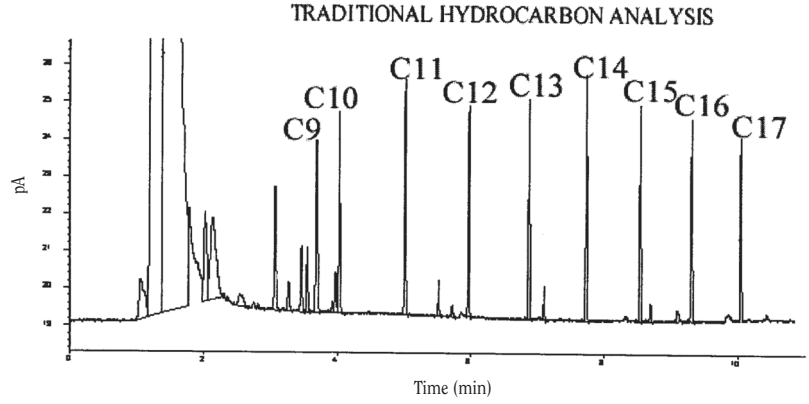


**Figure 1**. Traditional GC analysis of hydrocarbons. Conditions: 10 min on DB-5 (15 m × 0.25 mm, 0.25-µm $d_f$).

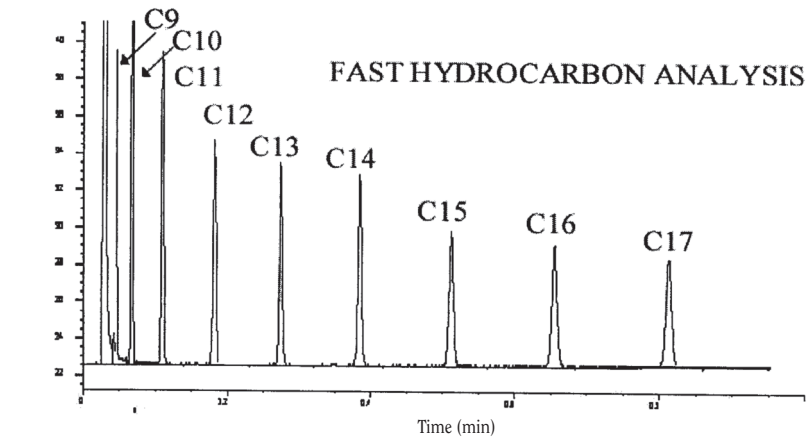


**Figure 2.** Fast GC analysis of hydrocarbons. Conditions: column, 1.8 min on HP-5 (1 m × 0.1 mm, 0.17-µm $d_f$); temperature program, 85°C for 0.1 min, to 115°C at 95°C/min, to 150°C at 65°C/min.

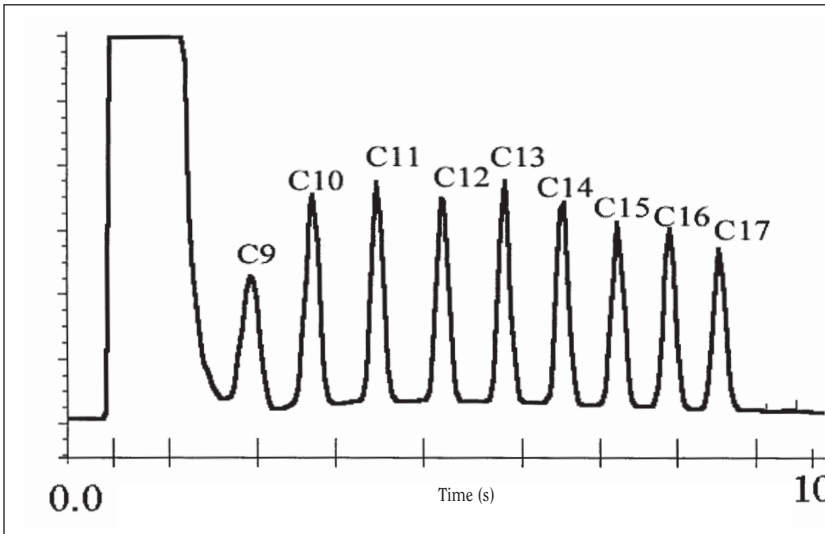


**Figure 3.** EZFlash analysis of hydrocarbons. Conditions: 10 s (5 m × 0.32 mm, 0.25-µm $d_f$), 60°C, 19.2°C/s.

## Results and Discussion

The following results demonstrate the effects of rapid temperature programming on various sample types. Figure 1 is an analysis of the hydrocarbon sample on the HP model 6890 GC operated in the traditional way. This analysis of normal hydrocarbons (nonane through heptadecane) was done using an HP-5 column (15 m × 0.25 mm, 0.25-µm $d_f$). The total analysis time was 9.3 min. This chromatogram had been generated earlier in our lab for an industrial project. Figure 2 is a chromatogram of the analysis of the same hydrocarbon sample on the 240 V HP 6890 GC operating at its maximum oven temperature programming rates. The column used for this analysis was an HP-5 column (1 m × 0.1 mm, 0.17-µm $d_f$). The total analysis time was 0.81 min, an 11-fold improvement in time. Finally, Figure 3 is the same analysis done using an EZFlash accessory in an HP model 5890 GC using an Rtx-5 column (5 m × 0.32 mm, 0.25-µm $d_f$). Normal hydrocarbons (nonane through heptadecane) were baseline resolved in 9 s. The oven temperature programming rate was 19.2°C/s. Table I is a comparison of the retention times and resolutions for all peaks for each of the 3 analysis conditions. The average resolution is 24 for the 15-m column, 10 for the 1-m column, and 2.5 for the 5-m EZFlash column. This is obviously a very easy sample, and fast temperature programming shows drastic improvements in the analysis time.

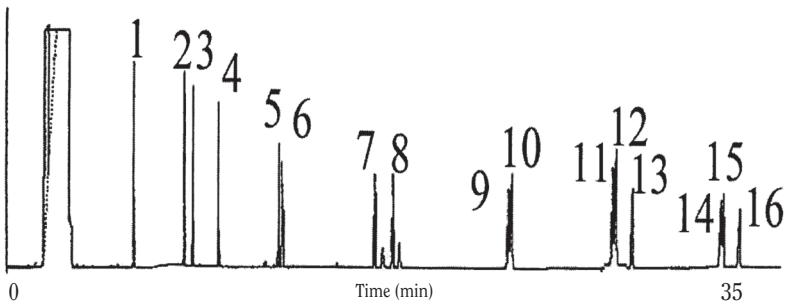


**Figure 4.** Traditional analysis of PAHs. Conditions: 35 min on PE-1 (30 m × 0.25 mm, 0.25-µm $d_f$).

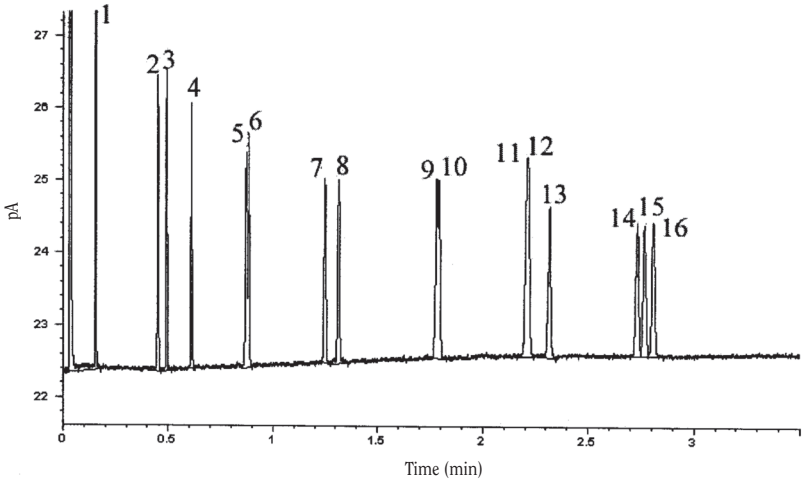


**Figure 5.** Fast GC analysis of PAHs. Conditions: 3 min on HP-5 (1 m × 0.1 mm, 0.17-µm $d_f$).

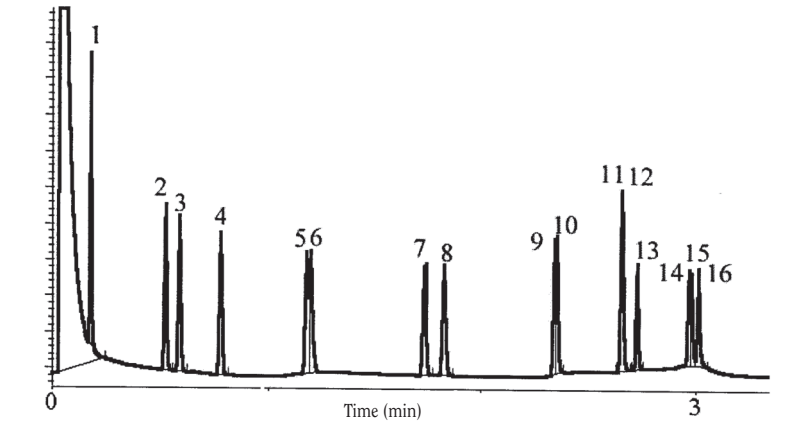


**Figure 6.** EZFlash analysis of PAHs. Conditions: column, Rtx-5 (5 m × 0.32 mm, 0.25-µm $d_f$); temperature program, 100 to 250°C at 50°C/min, to 325°C at 325°C/min and held 0.3 min; injection, 0.5 µL; split ratio, 60:1.

The next sample is a polycyclic aromatic hydrocarbon (PAH) sample. Figure 4 shows the analysis of 16 PAHs on a PE-1 column (30 m × 0.25 mm, 0.25-µm $d_f$). This chromatogram was published in the Ph.D. thesis of Wang (11). The analysis of the 16 PAHs was done on the PE Autosystem XL GC and was complete in 35 min. Figure 5 is the same PAH sample analyzed on the 240 V HP 6890 GC in less than 3 min using an HP-5 (1 m × 0.1 mm, 0.17-µm $d_f$). Figure 6 is the PAH sample analyzed on the 5890 GC using an Rtx-5 EZFlash column (5 m × 0.32 mm, 0.25-µm $d_f$) in 3 min. Because of several peak pairs that are difficult to separate, the extra-fast temperature capability does not show any improvement. Table II lists the retention times and resolutions of the 16 PAHs for each of the 3 methods. The 30-m column gives the best results; however, 3 of the peak pairs have a resolution of less than 1.5. The 1-m column resolves all but 2 of the peaks; however, 3 of the remaining peak pairs have a resolution of less than 1.5. Interestingly, the next to last peak pair has a greater resolution on the 1-m column than on the 30-m column. The 5-m EZFlash column resolves all but 1 peak; however, 3 peak pairs have a resolution of less than 1.5. Depending on the pur-

pose of the analysis, this loss of resolution may or may not be acceptable. The use of selective ion monitoring (SIM) in GC–mass spectrometry (MS) will provide spectrometric resolution of these peaks in most cases.

Chewing gum, breakfast cereals, and granola bars are more typical commercial samples. Prior to the analysis of these samples, it was necessary to extract the analyte. The samples were extracted using MAE as previously described. The extract was analyzed using the EZFlash system. Figures 7–9 are chromatograms of the extracts of each sample type. The BHT peak and the internal standard (naphthalene) peak are noted on each chromatogram. Table III shows the results for each sample and the corresponding precision data for the retention times.

The final figure is an analysis of perfumed mineral oil used to make gel candles. Figure 10 shows a fast analysis of this sample. The analysis is done using the HP 5890 with an EZFlash attachment on an Rtx-5 column (5 m × 0.32 mm, 0.25-µm $d_f$). This is an ideal sample type to analyze with this instrumentation, because it has the highly volatile perfume peaks and the much less volatile mineral oil peaks. The analysis of the same sample on the 240 V HP 6890 with an HP-1 (8 m × 0.25 mm, 0.25-µm $d_f$) took 9 min, and a traditional analysis using a 5890 GC with a 30-m column took 50 min. With the fast temperature program, the analysis time was 2 min. Tables IV and V show the precision in the retention times and the peak areas for several peaks in Figure 10. The goal was to quantitate the level of perfumes in the gel candles with no interest in the *n*-paraffin peaks. These results were obtained using manual

**Table I. Retention Time and Resolution Comparisons for Hydrocarbon Analysis on the 5-m EZFlash, 1-m Fast, and 15-m Conventional Columns**

| | Retention time (min) | | | Resolution | | |
|---|---|---|---|---|---|---|
| | 5 m | 1 m | 15 m | 5 m | 1 m | 15 m |
| $C_9$ | 0.040 | 0.046 | 3.102 | 4.67 | 4.87 | 8.40 |
| $C_9$–$C_{10}$ | 0.054 | 0.067 | 4.073 | 2.33 | 5.08 | 23.82 |
| $C_{10}$–$C_{11}$ | 0.068 | 0.109 | 5.063 | 2.93 | 8.38 | 27.81 |
| $C_{11}$–$C_{12}$ | 0.083 | 0.181 | 6.018 | 2.93 | 11.40 | 28.08 |
| $C_{12}$–$C_{13}$ | 0.097 | 0.274 | 6.924 | 2.80 | 12.37 | 26.97 |
| $C_{13}$–$C_{14}$ | 0.110 | 0.384 | 7.780 | 2.60 | 12.67 | 26.55 |
| $C_{14}$–$C_{15}$ | 0.122 | 0.512 | 8.590 | 2.40 | 12.39 | 24.74 |
| $C_{15}$–$C_{16}$ | 0.133 | 0.654 | 9.358 | 2.27 | 11.31 | 23.87 |
| $C_{16}$–$C_{17}$ | 0.144 | 0.812 | 10.086 | 2.13 | 11.02 | 22.17 |

**Table II. Retention Time and Resolution Comparisons for PAH Analysis on the 5-m EZFlash, 1-m Fast, and 30-m Conventional Column**

| | Retention time (min) | | | Resolution | | |
|---|---|---|---|---|---|---|
| | 5 m | 1 m | 30 m | 5 m | 1 m | 30 m |
| 1 | 0.18 | 0.16 | 6.15 | — | — | — |
| 1–2 | 0.53 | 0.45 | 8.66 | 24.49 | 39.95 | 52.93 |
| 2–3 | 0.60 | 0.49 | 9.91 | 3.39 | 4.45 | 7.99 |
| 3–4 | 0.79 | 0.61 | 10.41 | 9.17 | 11.55 | 22.90 |
| 4–5 | 1.19 | 0.87 | 13.43 | 17.87 | 21.62 | 43.50 |
| 5–6 | 1.21 | 0.88 | 13.63 | 0.81 | 0.95 | 2.37 |
| 6–7 | 1.74 | 1.25 | 18.27 | 21.97 | 26.47 | 54.81 |
| 7–8 | 1.83 | 1.32 | 19.14 | 3.68 | 4.33 | 9.25 |
| 8–9 | 2.34 | 1.78 | 24.79 | 23.72 | 16.20 | 48.29 |
| 9–10 | 2.35 | — | 24.96 | 0.55 | nr* | 1.26 |
| 10–11 | 2.66 | 2.22 | 29.67 | 14.54 | 10.75 | 35.40 |
| 11–12 | — | — | 29.79 | nr | nr | 1.02 |
| 12–13 | 2.73 | 2.32 | 30.89 | 3.50 | 3.33 | 9.45 |
| 13–14 | 2.97 | 2.73 | 35.25 | 15.09 | 16.21 | 30.32 |
| 14–15 | 2.98 | 2.77 | 35.37 | 0.63 | 1.39 | 0.85 |
| 15–16 | 3.01 | 2.81 | 36.18 | 1.89 | 1.65 | 5.71 |

* nr, not resolved.

**Table III. Percent Relative Standard Deviations (%RSDs) of Calculated Amounts and Retention Times for BHT in Various Food Products***

| | BHT (ppm) | % RSD | Retention time (min) | % RSD |
|---|---|---|---|---|
| Granola bar | 23 | 4.3 | 0.735 | 0.08 |
| Chewing gum | 108 | 2.8 | 1.055 | 0.09 |
| Breakfast cereal | 9 | 1.1 | 0.746 | 0.08 |

* Analysis was done using the EZFlash attachment on the HP 5890 GC. Quantitation was done using the internal standard method with a 5-point calibration curve ($n$ = 3).

**Table IV. Reproducibility of Retention Times for Various Peaks in Figure 10**

| | ISTD | Peak 1 | Peak 2 | Peak 3 |
|---|---|---|---|---|
| Trial 1 | 0.196 | 0.320 | 0.850 | 0.949 |
| Trial 2 | 0.197 | 0.320 | 0.850 | 0.949 |
| Trial 3 | 0.197 | 0.321 | 0.851 | 0.949 |
| Mean | 0.196 | 0.320 | 0.850 | 0.949 |
| Standard deviation | 0.00058 | 0.00058 | 0.00058 | 0 |
| **%RSD** | **0.29** | **0.2** | **0.07** | **0** |

**Table V. Reproducibility of Peak Areas for Various Peaks in Figure 10**

| | ISTD | Peak 1 | Peak 2 | Peak 3 |
|---|---|---|---|---|
| Trial 1 | 35126 | 3979 | 2967 | 4134 |
| Trial 2 | 36330 | 4127 | 2979 | 3922 |
| Trial 3 | 34199 | 3907 | 2999 | 4168 |
| Mean | 35728 | 4053 | 2973 | 4028 |
| Standard deviation | 851 | 105 | 8.5 | 150 |
| **%RSD** | **2.4** | **2.6** | **0.29** | **3.7** |

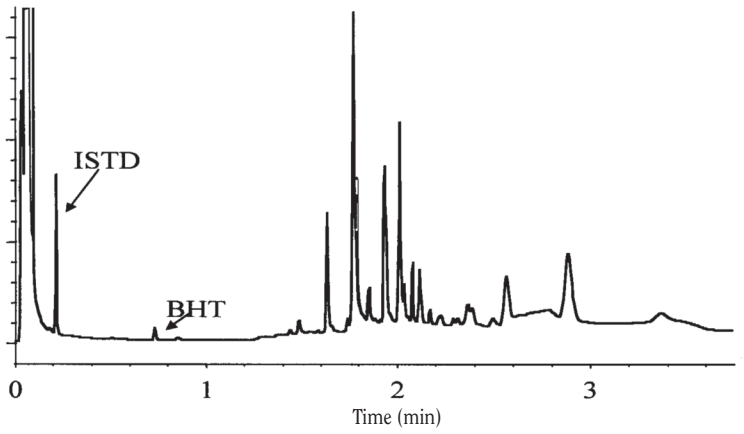


**Figure 7.** Fast analysis of a granola bar for BHT. Conditions: column, Rtx-5 (5 m × 0.32 mm, 0.25-µm $d_f$); temperature program, 100 to 300°C at 100°C/min and held for 1.5 min; injection, 1 µL; split ratio, 23:1.

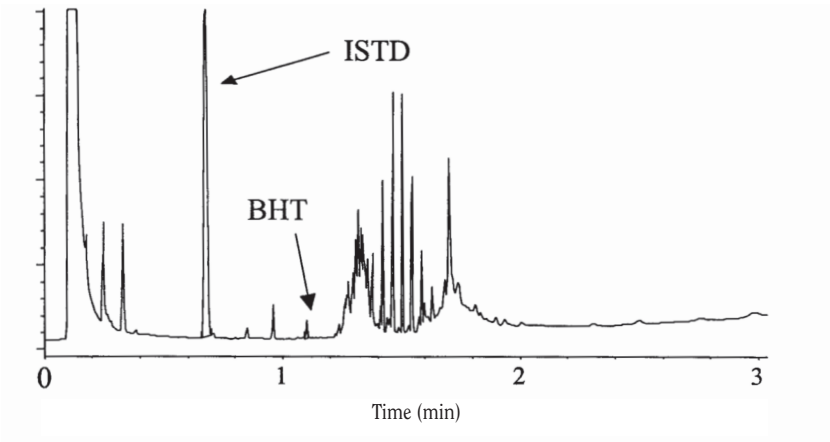


**Figure 8**. Fast analysis of chewing gum for BHT. Conditions: column, Rtx-5 (5 m × 0.32 mm, 0.25-µm $d_f$); temperature program, 85°C increased 63°C/min for 40 s, to 300°C at 130°C/min, held for 1.5 min; injection, 1 µL; split ratio, 31:1.

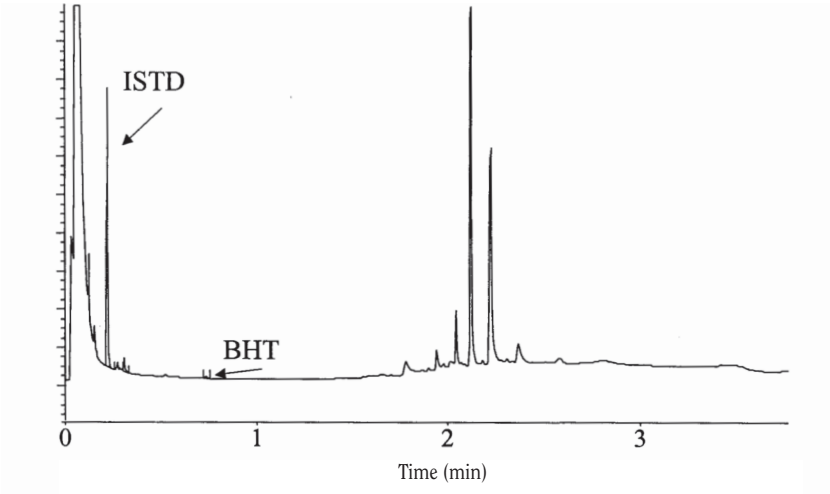


**Figure 9**. Fast analysis of breakfast cereal for BHT. Conditions: column, Rtx-5 (5 m × 0.32 mm, 0.25-µm $d_f$); temperature program, 100 to 300°C at 100°C/min, held for 1.5 min; injection, 1 µL; split ratio, 23:1.

injections; an autosampler will produce data that is as good or better than this data.

## Conclusions

It has been is shown that fast GC can significantly reduce the analysis time of many sample types. It was possible to reduce the analysis times of the 4 different sample types in this work compared with previously published chromatograms. Speeding up the analysis does decrease the resolution of the peaks. However, the loss of resolution does not greatly affect the analysis time for simple samples and some complex samples. The analysis time of the PAH sample, for example, was shortened using fast GC, but 2 peak pairs were no longer resolved on the 1-m column. It appears that many published GC methods could easily be done in much less time, although not all samples are amenable to a fast analysis. There must be a compromise between speed and resolution, and where that compromise lies depends on the requirements of the analysis. Many times, a loss of resolution is acceptable. The loss of chromatographic resolution can be even more acceptable if the detector is an MS, where SIM mode can be used to spectrometrically resolve peaks. Faster analyses are possible by using the EZFlash attachment to the GC. This faster temperature programming makes it possible to perform a rapid analysis for a sample that contains analytes with a wide range of boiling points in a short amount of time. This is demonstrated for various types of samples in this work.

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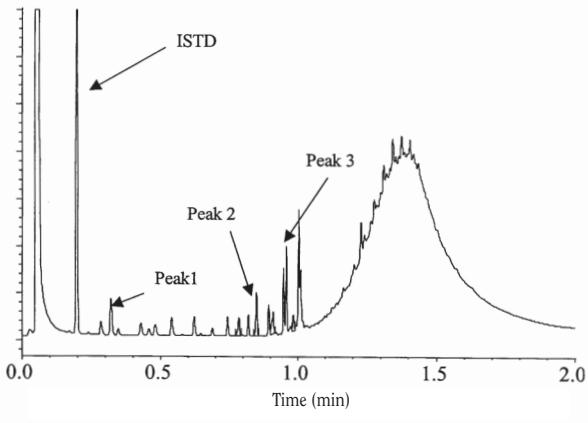


**Figure 10.** Fast analysis of a gel candle. Conditions: column, Rtx-5 (5 m × 0.32-mm i.d., 0.25-µm $d_f$); temperature program, 70 to 100°C at 60°C/min, to 200°C at 240°C/min, to 325°C at 250°C/min and held 35 s; injection, 1 µL; split ratio, 40:1.

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