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# Measurement of Organic Vapors at Sub-TLV® Concentrations Using Fast Gas Chromatography*

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**Gas chromatography usually is considered too slow a method to be useful for real-time or near real-time monitoring. If the chromatographic system is optimized for speed, however, it is possible to reduce retention times significantly. Recently, a fast gas chromatograph (GC) was described that allows many simple separations to be completed in 10 sec or less. The system features a gas-cooled, electrically heated, capillary cold trap that focuses the sample as an extremely narrow band at the front of the column. In this study the fast GC was used to measure the concentrations of benzene, toluene, and xylene in test atmospheres generated in the laboratory. The measurements then were compared to simultaneous measurements made with a conventional GC. At concentrations ranging from the threshold limit value (TLV®) to one-tenth of the TLV, the fast GC decreased retention times by a factor of 10- to 100-fold relative to the conventional GC, with no loss of precision or accuracy. These results indicate that it may be feasible to develop a high-speed monitoring system based on a GC design similar to the one in this study.**

Gas chromatography (GC) currently is used for ambient air monitoring in a number of industries. Often a centrally located GC is connected to a network of sampling lines through a multiport valve and is used to analyze sequentially samples collected from various areas. Because a single GC separation normally requires several minutes or more, the cycle time for a multipoint sampler easily can exceed an hour. While this type of apparatus provides information on air quality at a relatively low cost, it is not suitable for applications where real-time, or near real-time, monitoring is required.

GC, however, is potentially a much faster method of separation than usually is realized. If the chromatographic system is optimized for speed rather than resolution, it is possible to achieve relatively simple separations in as little as a few seconds. The feasibility of performing such high-speed separations was first demonstrated by Desty,[1] who, in 1965, separated 15 components in under 2 sec. Since Desty's initial work, a number of publications have appeared that discuss both the theoretical and practical aspects of fast gas chromatography.[2-8] While these studies have shown that high-speed separations are possible, the techniques they describe generally have been complex and have not been applied to routine environmental monitoring.

The major barrier preventing application of high-speed techniques to routine analysis has been a lack of suitable equipment. For fast GC to be successful, the peak widths must be kept as narrow as possible. In particular, extra-column band broadening caused by the injector, detector, and connectors must be minimized. The importance of preventing band broadening is illustrated by a comparison of final peak widths in conventional and fast GC. In conventional GC, peak widths usually are measured in seconds or tens of seconds. In fast GC, peaks are much narrower, often 50 msec or less. It can be shown that in order to produce a final peak this narrow, the initial band width produced by the inlet should be no more than about 20 msec.[9]

Conventional GC inlets that use syringe injection and a splitter typically produce initial band widths of 50 to 100 msec, and are clearly inadequate for high-speed separations. Gas injection systems, using a rotary valve and sampling loop, are likely to produce even wider injection bands, often measuring 1 to 10 sec or more. Even for normal-speed chromatography, gas sampling systems of this type may be inadequate and often require that the sample be focused on the front of the column, or on a pre-column, to improve resolution and limits of detection.[10]

In addition to the requirement for an extremely narrow injection band, a fast GC system must feature a detector and column connections that have extremely low dead volumes to minimize band broadening in those areas, and the electronics must have millisecond response times. In most cases, commer-

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cially available equipment is not able to meet these demands. Detectors that use a closed cell—such as thermal conductivity, electron capture, or photoionization—are especially susceptible to peak spreading caused by dead volumes and usually are not appropriate for high speed applications. Flame ionization detectors (FID) have little or no dead volume and, if the column is moved close to the base of the flame, can be used for fast GC. While most FIDs, therefore, can be adapted to fast GC, most electrometers are not capable of accurately tracing peaks as narrow as those developed by high speed systems.[11] Until recently, there also was a lack of affordable high-speed data collection and processing systems. Advances in the areas of personal computer technology and electronics now have made it feasible to collect and process data at rates that are adequate for fast GC applications.

Recent publications from one of the authors' laboratories describe a GC that is capable of meeting the requirements of high-speed analysis.[12,13] The inlet uses a metal capillary cold trap to focus and concentrate the sample before it enters the column. The trap is cooled by a continuous flow of cold nitrogen and is heated resistively for reinjection with a low voltage, high current pulse from a capacitor discharge power supply. Using the cold trap inlet with thin film capillary columns, an FID, and specially designed electronics, the authors were able to analyze simple mixtures of liquids in less than 10 sec.[12]

This same instrument also may be useful as a direct air inlet and sampling system for monitoring organic vapors. In this paper, the results of a preliminary study concerning the application of high speed GC to the measurement of aromatic vapors in air at threshold limit value (TLV®) and sub-TLV concentrations are reported.

## EXPERIMENTAL MATERIALS AND METHODS

### Experimental Apparatus

The design of the fast GC is shown schematically in Figure 1. Various components of the system are described in the following paragraphs.

Samples were introduced using a motor-driven, six-port valve (Valco Instruments Co., Inc., Houston, Tex.) fitted with a 200-$\mu$l sampling loop. The outlet of the six-port valve was connected to a 50-cm long buffer column made from 0.25-mm i.d. deactivated, fused silica tubing (Quadrex Corporation, New Haven, Conn.). The buffer column was enclosed in an aluminum chamber which was heated to 75° C to prevent sample condensation in that area. The downstream end was attached to a 15-cm long capillary cold trap made from 0.25-mm i.d. × 0.625-mm o.d. Monel® 400 tubing. The trap tubing was coiled slightly to allow for length changes associated with heating and cooling and was enclosed in a 9-cm long chamber made of Teflon.® The chamber was cooled to -60° C by a continuous flow of cold nitrogen gas. The nitrogen was cooled by running it through a copper coil submerged in liquid nitrogen.

At each end of the Teflon® chamber, the trap tubing was clamped between two copper blocks which served as electrical contacts during the heating cycle. The copper blocks were heated to 100° C with 150 W heating cartridges to prevent sample condensation outside the cold trap.

During the trapping cycle, which lasted for 15 to 30 sec, sample vapors were collected by condensation on the inner wall of the trap tubing. The frozen sample was then rapidly vaporized to form a narrow injection band by running a short pulse of current through the trap tubing. The current was provided by a capacitor discharge power supply which is capable of raising the

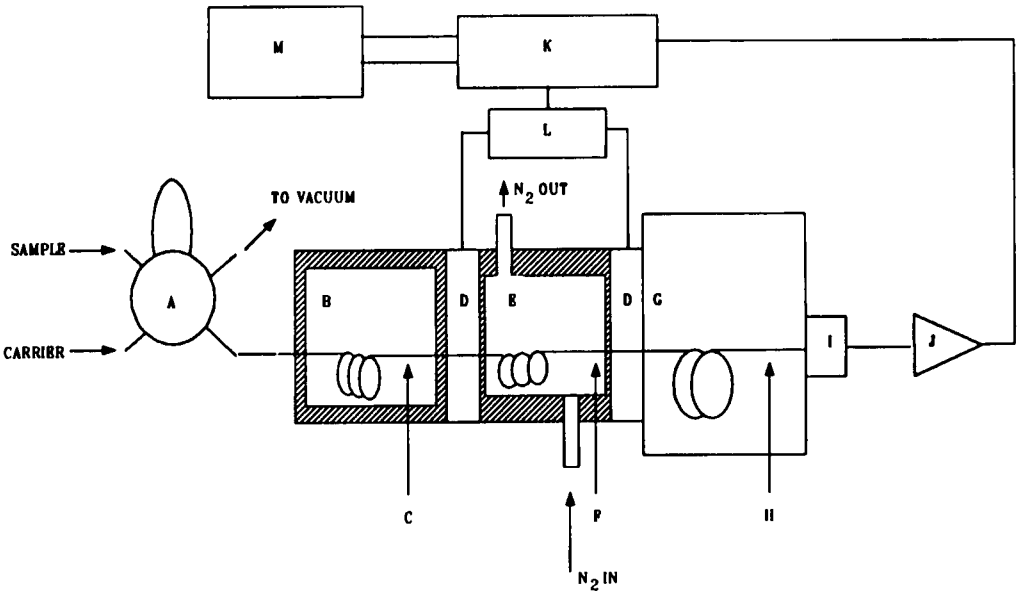


Figure 1—Diagram of the fast GC system. (A) Six-port rotary valve; (B) heated buffer chamber; (C) buffer column; (D) heated copper electrodes; (E) cold trap chamber; (F) capillary cold trap; (G) oven; (H) capillary column; (I) flame ionization detector; (J) fast electrometer; (K) A/D and D/A converter; (L) capacitor discharge power supply; (M) computer.

trap temperature by as much as 300° C in less than 20 msec. The trap temperature was monitored by wrapping a 36-guage, type J thermocouple around the trap tubing. Details of the inlet system design and performance characteristics have been presented elsewhere.[12,13]

The high-speed inlet was mounted on an HNU model 301 GC (HNU Systems, Inc., Newton, Mass.). All separations were performed using isothermal analysis at temperatures of 50 to 70° C. The column was a 5-m long, 0.25-mm i.d. capillary, with a 0.1-$\mu$m bonded methyl silicone stationary phase (Quadrex). Hydrogen was used as the carrier gas in all experiments and was provided at flow rates ranging from 3 to 5 mL/min to produce average linear velocities ranging from about 175 to 275 cm/sec.

Peaks were detected using a standard HNU Systems FID with the column moved foward to the base of the flame to minimize the effective dead volume. The FID signal was directed to a fast electrometer - amplifier with a response time of 5 msec. The high-speed electronics were developed specifically for this application by HNU Systems. Data were digitized and the entire system was controlled using a 12-bit analog to digital—digital to analog converter (DT2801, Data Translation, Inc., Marlboro, Mass.) mounted in a 80286 based personal computer. Data were collected at a frequency of 400 Hz using Labtech Notebook® software (Laboratory Technologies Corporation, Wilmington, Mass.), and analysis was performed using software developed in the authors' laboratory.

The test atmospheres used in this study contained benzene, toluene, and xylene at concentrations ranging from the TLV to one-tenth the TLV. The relative humidity was adjusted to levels ranging from 10% to 80%.

The design of the vapor generator and monitoring system is shown schematically in Figure 2. The monitoring system has been described in detail elsewhere.[14] In brief, the vapors were generated by controlled introduction of a test mixture from a liquid reservoir into an airstream of controlled flow rate, temperature, and humidity. The vapor concentration was controlled by adjusting the relative flow rates of the air and the liquid test mixture.

The concentration of benzene, toluene, and xylene was monitored continuously using a conventional GC vapor analysis system, featuring a Hewlett Packard 5890 chromatograph with a 30-m long, 0.32-mm i.d. capillary column and a DB-624 stationary phase. Peaks were detected using an FID. Samples were introduced through an electrically actuated capillary gas sampling valve (Valco) and were focused on a 1-ft long, 0.32-mm i.d. fused silica Poraplot Q® precolumn (Chrompack International, Middelburg, The Netherlands). The temperature was programmed to increase from 60° C to 150° C during the analysis. Total sampling and analysis time was about 6 min, and the time between successive samples was 10 min. Data from the conventional GC was collected and processed using an HP 3357 laboratory automation system. The conventional GC was calibrated using vapor injections from a set of static standards prepared in bags made of Saran® resin.

### Procedures

The vapor generator was adjusted to produce a test atmosphere containing benzene at approximately 10 ppm, and xylene and toluene at 100 ppm. After allowing the vapor concentration to stabilize, a series of simultaneous analyses was performed using both the conventional GC and fast GC, thus allowing a side-by-side comparison of the two systems. The vapor concentration then was reduced in a stepwise manner, and the experiment was repeated at various concentrations. Initial experiments were run at a relative humidity of 10% and then repeated at relative humidities as high as 80%.

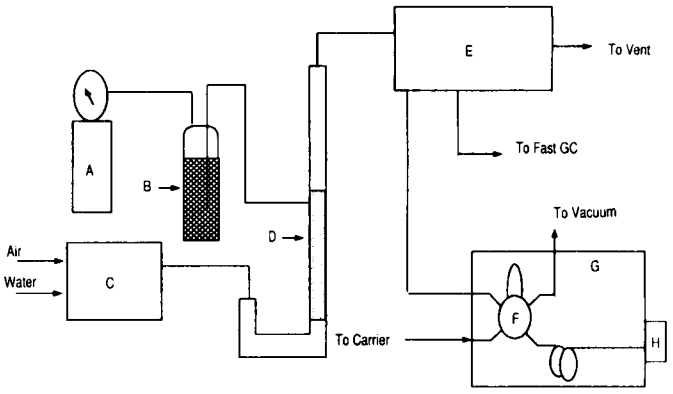


Figure 2—Diagram of the vapor generator and test apparatus. (A) Pressure-regulated $N_2$ supply; (B) test mixture reservoir; (C) flow, temperature, and humidity controller for dilution air; (D) mixing and vaporization chamber; (E) vapor sampling chamber; (F) six-port rotary valve; (G) conventional GC oven; (H) flame ionization detector.

## RESULTS AND DISCUSSION

For a fast GC system to be useful in routine air monitoring, the quality of the analytical data should be comparable to that obtained with a standard GC. Among the important parameters considered in this study were the chromatographic resolution, the accuracy and precision of peak area and height measurements, retention time reproducibility, and the effect of water vapor on system performance.

The initial consideration in this work was the quality and speed of the chromatograms that could be obtained. Figure 3 shows chromatograms made with the standard GC and with the fast GC at a vapor concentration equal to approximately one-tenth the TLV for each component. The relative humidity was 10% in both cases. The conventional chromatogram shows retention times ranging from 2.25 min for benzene up to 3.7 min for o-xylene. The fast GC achieved a similar separation with a maximum retention time of about 6.2 sec. The distance between adjacent peaks in the high-speed chromatogram is still relatively large, indicating that the retention times could have been made even shorter without a significant loss of resolution. In addition to the difference in retention times, the peaks produced by the fast chromatograph generally show less tailing. Other than those differences, the two chromatograms appear to be essentially identical. These results indicate that, for simple mixtures, use of the high-speed chromatograph does not produce a significant loss of resolution.

In addition to producing adequate separations, a useful air monitoring GC system also must be accurate and should have a linear response over a wide concentration range. In order to

assess the fast GC's linearity over the range of test concentrations and to allow comparison of measurements made with the two systems, peak areas measured from the fast chromatograms were plotted against the vapor concentrations measured using the standard GC. The results are presented in Figure 4, where each point represents the average of three measurements made with conventional GC and seven to nine measurements made with the fast GC. Vertical error bars represent ±1 standard deviation for fast GC and horizontal error bars indicate ±1 standard deviation for conventional GC.

For each compound, the line shown in Figure 4 represents the least squares line of best fit, and in each case, the correlation coefficient is 0.99 or better. The high correlation coefficients, near 1.0, indicate that the two methods are in excellent agreement at concentrations ranging from approximately the TLV to one-tenth the TLV.

As indicated by the error bars shown in Figure 4, peak area measurements made from the fast chromatograms show a level of precision comparable to those obtained with the conventional system. Precision, or reproducibility, of concentration measurements, can be expressed as the relative standard deviation for either peak area or peak height measurements. These values are presented in Table I. For benzene concentrations ranging from 1 to 10 ppm and for toluene and o-xylene concentrations ranging from 10 to 90 ppm, the relative standard deviations for peak area ranged from ±3% to ±7%. Relative standard deviations for peak height also ranged from ±3% to ±7%. These results compare favorably with peak area measurements taken from the conventional GC, which also produced relative standard deviations ranging from ±3% to ±7%. Although these data should be considered preliminary, they indicate that the fast GC achieves precision and accuracy comparable to conventional GC.

Although retention time is not a reliable indicator of peak identity in the analysis of unknowns, it often is used in air monitoring applications where the number of peaks is limited and the composition of the mixture being separated is well defined. The reproducibility of retention time data, therefore, is an important consideration for air monitoring applications. In order to determine retention time reproducibility, a series of 20 replicate chromatograms was run over a 2-hr period. Toluene and o-xylene, with average retention times of 4.58 and 5.91 sec, both had relative standard deviations of ±0.6%. Benzene, with

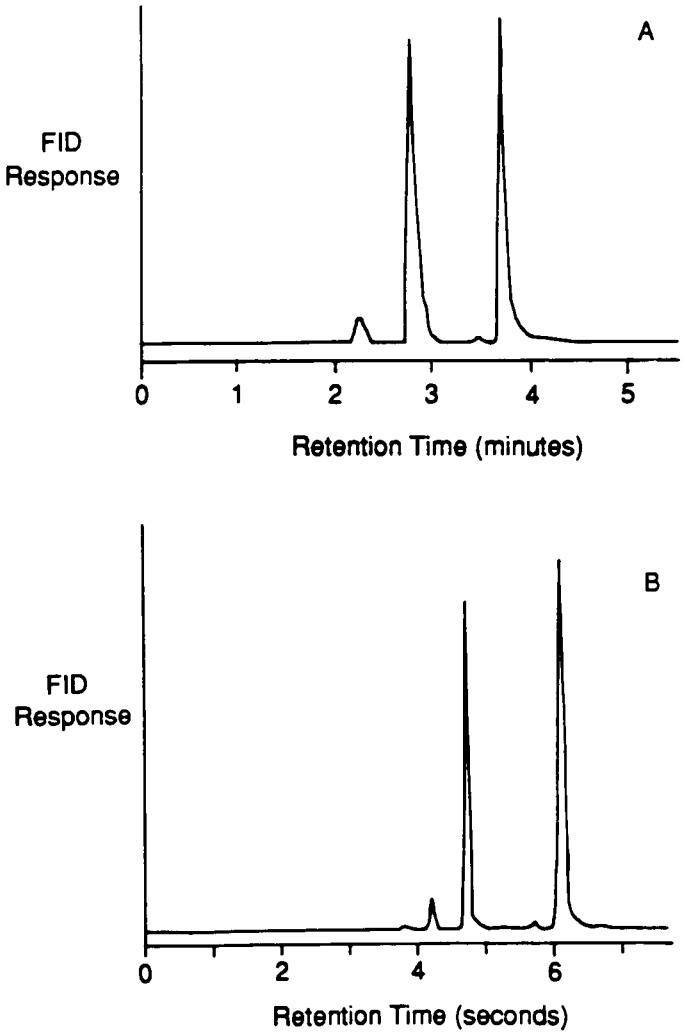


Figure 3—Comparison of a conventional chromatogram (A) and a fast chromatogram (B) run under similar conditions. Peak identities and concentrations are (1) benzene 1 ppm; (2) toluene 10 ppm; (3) O-xylene 10 ppm.

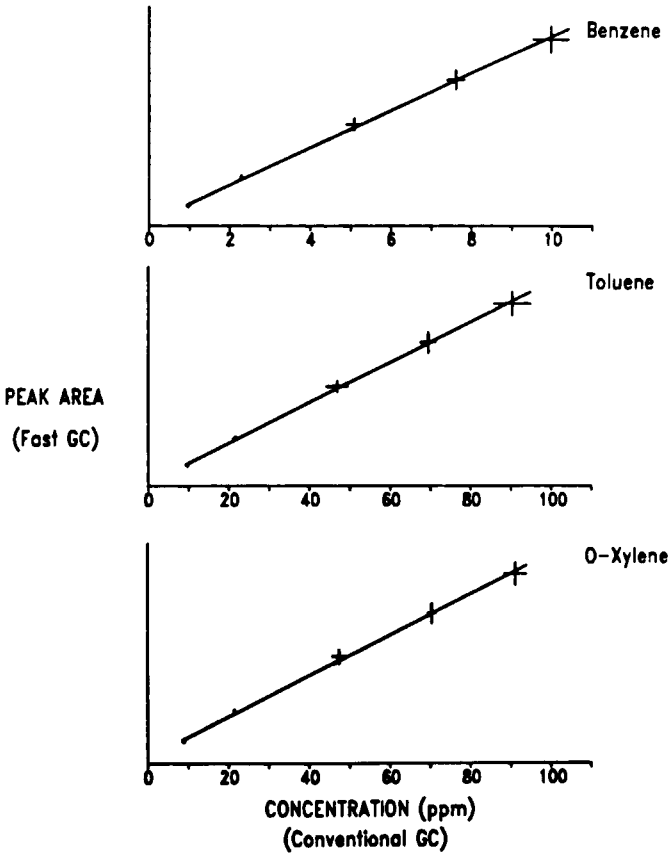


Figure 4—Peak area measurements from high-speed chromatograms (vertical axis) versus vapor concentration measured with conventional GC (horizontal axis). Each point represents the average of three conventional GC measurements and five to nine high-speed measurements. Error bars indicate one standard deviation. The straight lines represent the least squares line of best fit for each data set. In all cases the $R^2$ value is greater than 0.99.

an average retention time of 4.11 sec had a relative standard deviation of ±0.5%. These results indicate that retention time reproducibility is as good as that obtained with most conventional systems. The conventional system used in these experiments, for example, produced relative standard deviations of about 1%.

The final consideration in these preliminary tests was the possibility that water vapor would have a negative impact on the system performance. In many industrial environments, water vapor is likely to be present in the atmosphere at high concentrations. Because the high-speed inlet uses a capillary dimension cold trap, this was considered to be a potential problem. If a large amount of water was collected with the sample, ice forming on the inner wall of the trap could conceivably slow the revaporization process and degrade chromatographic performance. It was thought possible that, in an extreme case, ice might even block the flow of carrier gas.

In order to test the effect of water vapor on the system performance, chromatograms were run at relative humidities ranging from 10% to 80%. Sample chromatograms obtained at 10% and 80% relative humidity are shown in Figure 5. A comparison of peak areas, peak widths, and retention times obtained at high and low humidities indicates that, under these conditions, water vapor had no statistically significant effect on the performance of the system. This is confirmed by visual inspection of the chromatograms presented in Figure 5. The lack of any humidity effect is probably explained by the extremely small volume of the sample injection. The chromatograms used in this study were made with injection volumes of only 200 $\mu$L, which, at a relative humidity of 80% and a temperature of 25°C, would contain about 4 $\mu$g of water. At this level, water is expected to act much like any of the materials being analyzed and has little or no effect on the injection system or on chromatographic performance. If significantly larger sample volumes were used, it is possible that water would cause some difficulty. The results obtained in these experiments, however, indicate that the sensitivity is high enough so that significantly larger samples rarely would be necessary for monitoring in most industrial environments.

## CONCLUSIONS

Although the preliminary results presented in this paper are encouraging, there are a number of issues which have not yet been investigated. Among the potential limitations with the current design are the durability of the trap, the lack of a back-flush system to remove high boiling contaminants, the potential for thermal decomposition of the sample, the requirement for liquid nitrogen cooling, and a lack of efficient software for high-speed analysis of the data. In addition, other analytical concerns, such as the limits of detection and the long-term stability, have not been investigated yet.

Despite the need for further development, the results presented here do indicate that a high-speed GC system may be useful for air monitoring in some workplaces. A system of this type would be especially appropriate where the industrial hygienist is concerned with potential exposures to a limited number of volatile organics. In these situations, application of high-speed techniques may significantly reduce the lag time between measurements for single point monitors and the cycle time for multipoint monitors. This may allow GC systems to be used as monitors in situations where the longer analysis time associated with conventional GC is considered unacceptable.

**TABLE I**
**Relative Standard Deviation of Peak Area and Height Measurements**

| Benzene | | | Toluene | | | O-Xylene | | |
|---|---|---|---|---|---|---|---|---|
| Conc. (ppm) | Area | Height | Conc. (ppm) | Area | Height | Conc. (ppm) | Area | Height |
| 10.0 | 7 | 6 | 90 | 7 | 6 | 91 | 6 | 4 |
| 7.6 | 6 | 6 | 69 | 7 | 6 | 70 | 7 | 4 |
| 5.1 | 5 | 6 | 47 | 6 | 5 | 47 | 7 | 5 |
| 2.3 | 4 | 4 | 22 | 3 | 3 | 21 | 4 | 3 |
| 1.0 | 7 | 5 | 10 | 5 | 6 | 9 | 7 | 7 |

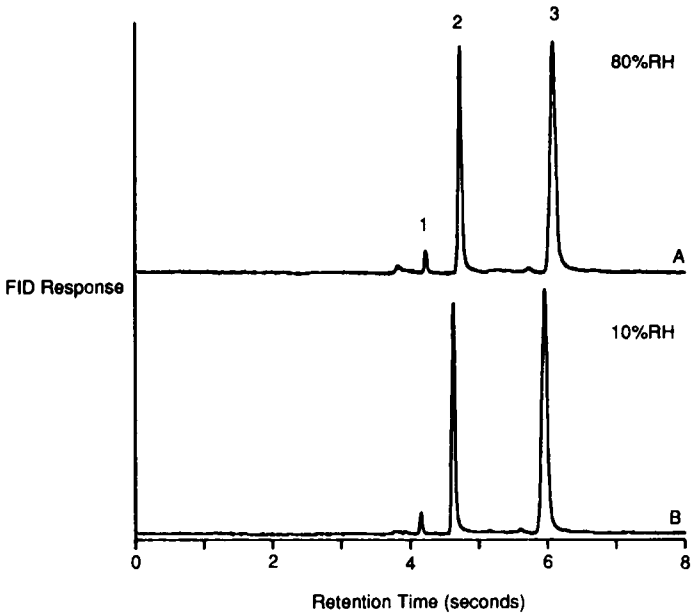


Figure 5—Comparison of fast chromatograms run at 10% RH (A) and 80% RH (B). Peak identities are (1) benzene; (2) toluene; (3) O-xylene.


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