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Original Paper

Performance characteristics of a new prototype for a portable GC using ambient air as carrier gas for on-site analysis

The performance characteristics of a portable GC instrument requiring no compressed gas supplies and using relatively lightweight transportable components for the analysis of volatile organic components in large-volume air samples are described. To avoid the need for compressed gas tanks, ambient air is used as the carrier gas, and a vacuum pump is used to pull the carrier gas and injected samples through the wall-coated capillary column and a photoionization detector (PID). At-column heating is used eliminating the need for a conventional oven. The fused silica column is wrapped with heater wire and sensor wire so that heating is provided directly at the column. A PID is used since it requires no external gas supplies and has high sensitivity for many compounds of interest in environmental air monitoring. In order to achieve detection limits in the ppb range, an online multibed preconcentrator containing beds of graphitized carbons and carbon molecular sieves is used. After sample collection, the flow direction through the preconcentrator is reversed, and the sample is thermally desorbed directly into the column. Decomposition of sensitive compounds during desorption is greater with air as the carrier gas than with hydrogen.

Keywords: At-column heating / Atmospheric air carrier gas / Portable GC / Semivolatile organic compounds / Vacuum-outlet GC

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1 Introduction

The analysis of volatile and semivolatile organic compounds (VOCs) at trace levels in air samples is of great interest because they are key components in industrial, environmental, indoor and outdoor air, and medical samples [1–5]. Sampling is typically performed offline followed by costly and tedious laboratory analysis using GC or GC-MS [3, 6, 7]. Nowadays, there is an increasing interest in developing lower cost, portable, and micro-fabricated vapor analysis systems that allow on-site VOCs monitoring, which can immediately detect a disturbance in process, environmental, or health conditions. Currently, the emphasis is on new column heating techniques requiring no convection oven [8–11], microscale inline preconcentrators and inlet devices [12], arrays of

partially selective sensors [13–18], and methods of micromachining to produce small and efficient columns [10, 19, 20].

While most of the GC instruments designed for on-site analysis require the use of compressed gases, both for the carrier gas and detector gas, some efforts have addressed the use of vacuum-outlet GC with air as the carrier gas and detection devices that require no on-board gas supplies [20–27]. This leaves electrical power as the only consumable and thus provides a high level of instrument autonomy. The application of vacuum column-outlet conditions is an attractive way to increase the speed of an analysis, especially for short- and/or wide-bore columns [21, 28–32]. The effect of operating short columns with a reduced outlet pressure results in decreased pressure throughout most of the column leading to an increase in the gas-phase diffusion coefficient. This increases the longitudinal diffusion term of the Golay equation but decreases the resistance to mass transfer term. This results in an increase in the optimum linear velocity for minimum plate height, allowing separations

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Abbreviations: PID, photoionization detector; **HC Trap**, hydrocarbon trap; **VOC**, volatile organic compound

* JMS would like to dedicate this paper to the memory of Professor Sacks.

to be conducted at almost the same chromatographic efficiency with shorter analysis times [28, 33, 34]. However, the use of air as the carrier gas poses several problems including relatively poor column efficiency at high carrier gas flows and rapid stationary phase decomposition at elevated temperatures. A detector that requires no additional gas supplies must be used for this purpose. Photoionization detectors (PID), which require no support gases, are commercially available, robust, and satisfactory for use with vacuum-outlet GC and ambient air as the carrier gas. In addition, PIDs are highly sensitive for aromatic compounds as well as other compound classes of interest in environmental monitoring.

Many organic compounds found in environmental samples are present at low concentrations, which make it necessary to incorporate a preconcentrator device in the design of a GC instrument for these purposes. Numerous sorption-based trap devices, which remove organic compounds from large-volume air samples, have been described [12, 35–40]. Thermal desorption is typically used to liberate the organic compounds from the trap. Sample loss, contamination, and decomposition are often associated with these preconcentration techniques, particularly when they are used offline. Recently an inline trap has been described that effectively reduces many of these problems [40, 41]. The device uses a multibed sorption trap consisting of three beds of different grades of graphitized carbons and one bed of carbon molecular sieves. The beds are arranged with the weakest adsorbent located at the upstream end of the trap and the strongest adsorbent at the downstream end during sample collection. The device quantitatively removes most of the VOCs from both dry and wet samples.

The work described here combines the use of a four-bed preconcentrator with at-column heating of a fused silica capillary column and a PID operated at reduced pressure to obtain a GC system compatible with the needs of on-site monitoring of large-volume atmospheric samples. Instrument design and performance are considered. These studies provide guidelines for the establishment of performance limits for ambient-air driven GC instruments for environmental applications.

2 Experimental

2.1 Apparatus

The complete system is shown in Fig. 1. Gas flow control through sorption trap T is provided by miniature valves V_1 and V_2 (Model LFVA1230113H, The Lee, Westbrook, CT). To collect a sample both valves are opened and vacuum pump VP_2 (Model UN86 KNI, KNF, Trenton, NJ) pulls the air sample through the trap at flow rates up to $80 \text{ cm}^3/\text{min}$. The solid-line arrow shows the direction of airflow during sample collection. After sample collection

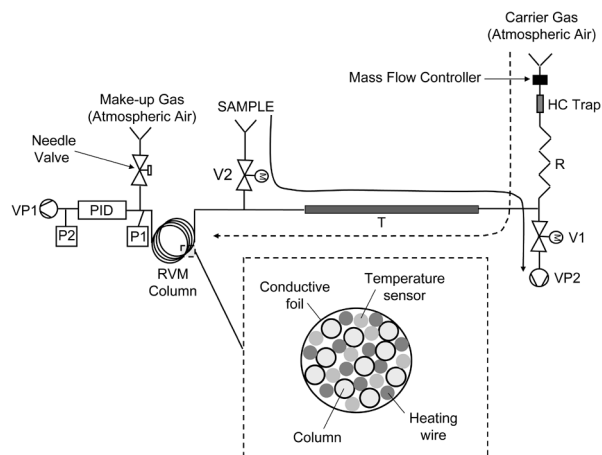


Figure 1. Diagram of the vacuum-outlet GC developed. Valves V_1 and V_2 are used to control the gas flow direction through the trap tube. The solid line from the sample source to the vacuum pump (VP_2) shows sample gas flow during preconcentration, and the dashed line shows carrier gas flow during desorption. Inset shows details of the RVM column assembly. Key: HC Trap, hydrocarbon trap; R, capillary restrictor; T, trap tube; P, pressure transducer; VP_1 , vacuum pump; P_1 and P_2 , pressure transducers.

is complete, both valves are closed, and vacuum pump VP_1 pulls carrier gas (ambient air) through the hydrocarbon trap (HC Trap), capillary restrictor R, trap T, the column, and the PID (dashed line arrow direction).

The multibed trap, heating process used for desorption and control circuitry has been described in detail [40]. The trap contains a grade ensemble of four different adsorbent materials ($2.2 \pm 0.1 \text{ mg}$ of each material were used) separated by quartz-wool plugs. It consists of a carbon molecular sieve (Carboxen 1000: mesh size 60/80; surface area $1200 \text{ m}^2/\text{g}$, density 0.44 g/mL) and three graphitized carbons (Carbopack X: mesh size 40/60; surface area $250 \text{ m}^2/\text{g}$, density 0.41 g/mL ; Carbopack B: mesh size 60/80; surface area $100 \text{ m}^2/\text{g}$, density 0.36 g/mL ; and Carbopack Y: mesh size 40/60; surface area $25 \text{ m}^2/\text{g}$, density 0.42 g/mL), all obtained from Supelco (Bellefonte, PA). Sampling and analysis flow need to be in opposite directions to avoid the highest-boiling-point components entering into contact with the strongest adsorbent (Carboxen 1000).

The use of the restrictor R (50-cm long \times 0.25-mm id deactivated fused silica tube) is needed to limit the flow of carrier gas to the VP_2 during sample collection, which would limit the sampling flow rate. An HC Trap is located in the inlet of the system to remove impurities from the atmospheric carrier gas. Two vacuum pumps were used in this study, but since the column flow is typically only about 2% of the flow through the trap during sample collection, a single vacuum pump can be used with only a small decrease in the sample-gas flow rate when the valves are open.

A 10.0-m long, 0.25-mm id fused silica wall-coated capillary column was wrapped with heater wire and sensor wire for at-column heating. The assembly was wound into a coil about 7 cm in diameter and wrapped in metal foil. The column assembly and the computer board used for column temperature control were manufactured by RVM Scientific (Santa Barbara, CA). Connecting lines with independent heating were provided by the manufacturer. The column used a 0.25- μm thick film of 5% phenyl, 95% dimethyl polysiloxane (DB-5, J&W Scientific, Folsom, CA).

The PID used in this study (Model PI 52-02A, HNU Systems, Newton Highlands, MA) has a cell volume <100 μL as stated by the manufacturer and used a 10.2-eV lamp. In order to increase flow rate through the PID, make-up gas (ambient air) is introduced into the gas flow from the column. A needle valve (Supelco) is used to control the make-up gas flow. Pressure transducer P_1 is used to monitor the pressure at the end of the separation column (outlet pressure, p_o) and pressure transducer P_2 is used to control the vacuum applied by the vacuum pump. Flow rate at the inlet of the carrier gas line was measured by a mass flow controller. All the component connections in the flow path from the sorption trap to the detector are low-dead-volume fused silica connectors and splitters (Supelco).

Monitoring of the desorption temperature was performed with a type-J thermocouple using 0.127-mm-id wire (36 AWG, Omega Engineering, Stamford, CT) attached to the outer wall of the trap tube. A PC equipped with a 16-bit A/D board (CIO-DAS16/F, Measurement Computing, Middleboro, MA) running Labtech Notebook software (Laboratory Technologies, Wilmington, MA) was used for data acquisition and instrument control. Chromatograms were processed with Grams/32 software (Galactic Industries, Salem, NH).

2.2 Materials and procedures

The compounds listed in Table 1 were used to challenge the preconcentrator and test the system. These compounds were chosen to include a variety of functionalities with consideration of the response characteristics of the PID. Saturated aliphatic hydrocarbons show a low response relative to the compounds in Table 1 and were not included in the test mixtures. One to two microliters of individual components were injected as liquids into 12 L Tedlar gas sampling bags (SKC, Eighty-Four, PA) and diluted with dry air. Humidified standards were prepared by using water-saturated air obtained by bubbling purified air through distilled water. Resulting vapor concentrations were in the range of 8–35 ppm v/v. The amount of sample challenging the sorption trap was controlled by the adjustment of the sample collection time.

3 Results and discussion

3.1 Operating conditions and extra-column band broadening

The use of vacuum-outlet GC with ambient air as the carrier gas provides for more autonomous instrument operation since only electrical power is consumable. However, the constraint of a one-atmosphere pressure drop through the system limits both average carrier gas velocity and volumetric flow-rate of the carrier gas at the column inlet. These limitations can affect the dead time of both the detector and the sorption-trap inlet as well as the column efficiency.

In conventional GC, variation of the inlet pressure is a convenient means for adjusting the average carrier gas velocity, u . However, in the work reported here, the pressure at the inlet of the carrier gas line is fixed at ambient pressure, which means that the column inlet pressure is slightly lower due to the pressure drop produced by the HC Trap, the restrictor, and the volatiles trap. Thus, the pressure drop through the column is smaller than one atmosphere, and average gas velocity and inlet flow rate reach upper limits as the outlet pressure is reduced. For the conditions used in this study, the maximum average carrier gas velocity is ~ 85 cm/s at the starting column temperature of $\sim 30^\circ\text{C}$, and the maximum inlet flow rate is ~ 1.8 cm³/min or 30 $\mu\text{L/s}$ (these parameters have been determined using the retention time of the less retained compound evaluated, acetone, as the hold-up time). Both these values decrease slightly with increasing temperature due to the increase in gas viscosity.

Figure 2 shows the effects of make-up gas and outlet pressure on the qualitative features of the chromatograms from the separation of a five-component mixture. For all the chromatograms the column temperature was 30°C for 60 s followed by a linear ramp of $10^\circ\text{C}/\text{min}$ to 150°C . Peak numbers correspond to compound numbers in Table 1. For chromatogram (a), outlet pressure p_o was 0.7 atm and no make-up gas was used. For chromatogram (b), p_o was maintained at 0.7 atm, and detector make-up gas (ambient air) was added at a flow rate of about 5 cm³/min at ambient pressure. For chromatogram (c), p_o was 0.25 atm, and no make-up gas was used. As indicated in the Section 2, the PID detector has a cell volume <100 μL , which makes it necessary to have a large volumetric flow rate through the detector to minimize the extra-column band broadening that is due to the cell volume of the detector. As can be seen in chromatogram (a), broad peaks with clear tailing appear when no make-up gas is added to increase the volumetric flow through the detector. Moreover, this results in inadequate resolution for peaks 3 and 4. The use of make-up gas in chromatogram (b), maintaining the same p_o as in chromatogram (a), allowed a larger volumetric flow in the detector. It

Table 1. List of compounds used in test mixtures. Experimental slopes with their confidence intervals ($\pm t \cdot s_{\text{slope}}$, $\alpha = 0.05$) and correlation coefficients (R^2) obtained for the log–log plots of the compounds evaluated in dry and humid conditions. Last column indicates whether decomposition of the target compound was detected when high temperature pulses ($>200^\circ\text{C}$) were applied for thermal desorption. The boiling points of the VOCs evaluated ranged from 56.2 to 179°C

| # | Name | Dry samples | | Humid samples | | Decomposition |
|----|------------------------------|-------------|--------|---------------|--------|---------------|
| | | Slope | R^2 | Slope | R^2 | |
| 1 | Acetone | 1.02 ± 0.05 | 0.9998 | 0.97 ± 0.05 | 0.9998 | Yes |
| 2 | Isoprene | – | – | – | – | Yes |
| 3 | 2-Butanone | 0.96 ± 0.06 | 0.9978 | – | – | Yes |
| 4 | 2-Pentanone | 1.03 ± 0.07 | 0.9959 | – | – | Yes |
| 5 | Benzene | 1.02 ± 0.02 | 0.9999 | 1.02 ± 0.02 | 0.9999 | No |
| 6 | Trichloroethylene | – | – | – | – | No |
| 7 | Toluene | 1.04 ± 0.05 | 0.9999 | – | – | No |
| 8 | 2-Hexanone | 1.04 ± 0.05 | 0.9994 | 1.06 ± 0.06 | 0.9991 | Yes |
| 9 | Hexanal | 1.03 ± 0.02 | 0.9958 | – | – | Yes |
| 10 | Tetrachloroethylene | 0.98 ± 0.07 | 0.9977 | – | – | No |
| 11 | Chlorobenzene | 1.00 ± 0.09 | 0.9953 | – | – | No |
| 12 | <i>m</i> -, <i>p</i> -Xylene | – | – | – | – | No |
| 13 | Styrene | 1.07 ± 0.10 | 0.9957 | – | – | Yes |
| 14 | <i>o</i> -Xylene | 1.01 ± 0.64 | 0.9979 | – | – | No |
| 15 | 2-Heptanone | 0.98 ± 0.08 | 0.9954 | 1.02 ± 0.03 | 0.9998 | Yes |
| 16 | α -Pinene | – | – | – | – | Yes |
| 17 | Heptaldehyde | 1.02 ± 0.04 | 0.9992 | – | – | Yes |
| 18 | Cumene | 1.03 ± 0.05 | 0.9988 | – | – | No |
| 19 | Benzaldehyde | 0.98 ± 0.13 | 0.9912 | 0.99 ± 0.07 | 0.9986 | No |
| 20 | β -Pinene | – | – | – | – | Yes |
| 21 | Limonene | – | – | – | – | Yes |
| 22 | 1,2-Dichlorobenzene | 1.04 ± 0.05 | 0.9997 | – | – | No |
| 23 | 1,2,3-Trimethylbenzene | – | – | – | – | No |
| 24 | 1,2,4-Trimethylbenzene | 1.09 ± 0.12 | 0.9948 | 1.00 ± 0.04 | 0.9996 | No |
| 25 | 3-Octanone | 1.03 ± 0.02 | 0.9958 | – | – | Yes |
| 26 | Butyraldehyde | – | – | – | – | Yes |
| 27 | 2-Carene | 1.02 ± 0.04 | 0.9998 | – | – | Yes |
| 28 | 3-Carene | – | – | – | – | Yes |
| 29 | γ -Terpinene | – | – | – | – | Yes |

resulted in more adequate chromatograms with much narrower and Gaussian peaks, and increased resolutions. Average carrier gas velocity in the separation column was equivalent in both cases as can be observed by the fact that the retention times for the five compounds did not show significant differences in the two chromatograms. The only disadvantage of the use of make-up gas in chromatogram (b) was the reduction in the peak areas due to the dilution of the compounds with the make-up gas. The band broadening observed in the chromatograms are mainly due to extra-column sources (preconcentration/injection and detector) due to the configuration of the system used. As indicated in Section 1, the performance of the preconcentrator inlet system and its effects on the band broadening of the peaks have been described in detail [40]. However, the results obtained in this study confirm that the PID dead volume has the greater effect on the efficiency of the separation system and the dead time of the sorption-trap inlet can be considered as negligible.

In chromatogram (c), the additional flow in the detector to reduce detector dead time was obtained by decreasing

p_o , without using make-up gas (*i.e.* by carrier-gas decompression). It resulted in larger average carrier gas velocities through the separation column and retention times were smaller by about a factor of two. Peak areas are comparable to those in chromatogram (b) due to the dilution from the increased flow in the PID. The resolution of peaks 3 and 4 in chromatogram (c) is poorer than in chromatogram (b). Peak shapes for the less retained compounds are equivalent to those in chromatogram (b). However, peak shape for the more retained compound (*i.e.* 3-octanone, # 25) is narrower and more Gaussian. These results indicate that the use of smaller p_o (*i.e.* increasing u) results in decreased resolution for the less retained compounds but increased efficiency for the more retained.

Quantitative data regarding the system's efficiency are shown in Fig. 3 (Golay plots) for the isothermal separation of 3-octanone (Fig. 3a) and 2-pentanone (Fig. 3b) at 36°C. The retention factor for these compounds at this temperature were 9.2 and 0.7, respectively. In order to ensure appropriate flows in the detector to minimize extra-column band broadening, make-up gas was used

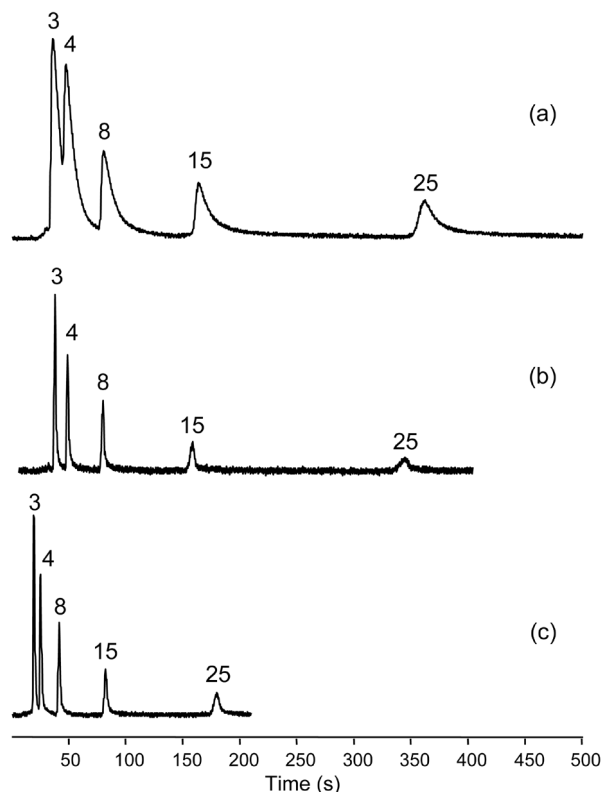


Figure 2. Chromatograms showing the effect of make-up gas and outlet pressure on the qualitative features in the separation of a five-component mixture. (a) $p_o = 0.7$ atm, no make-up gas; (b) $p_o = 0.7$ atm, make-up gas at $5 \text{ cm}^3/\text{min}$; and (c) $p_o = 0.25$ atm, no make-up gas. Peak numbers correspond to the compound numbers in Table 1.

when necessary. It allowed to evaluate different outlet pressures (measured by the P_1 pressure transducer in Fig. 1) meanwhile vacuum pressure (P_2 transducer) was maintained fixed at 0.2 atm. Each point represents the average of three injections at the indicated outlet pressure, and error bars show SDs. Model equations cannot be applied adequately in the system described because theoretical models not only use to neglect band broadening in the stationary phase, which is a reasonable approximation for the 0.25-mm id and 0.25- μm film column used here, but also neglect solute band broadening from extra-column sources, which is not the case in the developed system. The plot in Fig. 3b reflects that the minimum plate height for less retained compounds occurs with $\bar{u} \leq 55 \text{ cm/s}$, corresponding to a $p_o \leq 0.4$ atm. In these conditions, about 5500 plates are obtained from the system. For the more retained compounds (Fig. 3a), variations in the plate height at different average carrier gas velocities are small, and the minimum value occurs with a \bar{u} value of about 65 cm/s corresponding to a p_o value of 0.5 atm. These results suggest the use of average carrier gas velocities around 50–65 cm/s (p_o range of

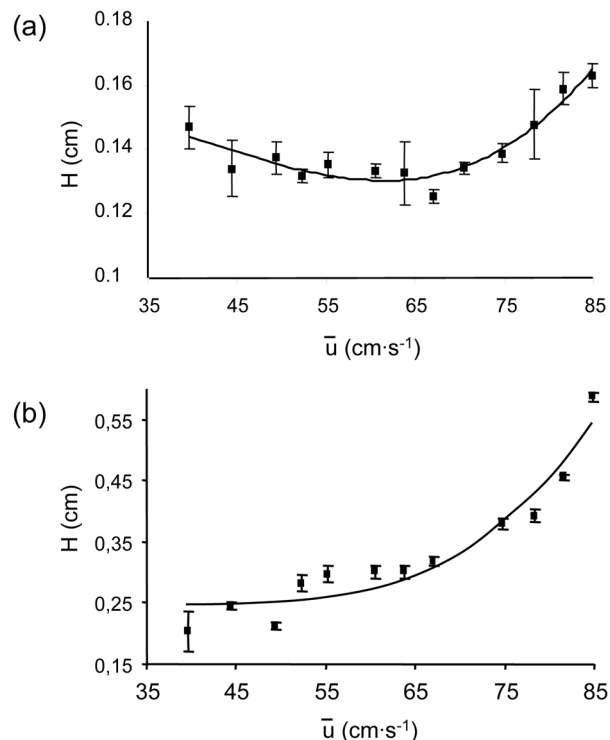


Figure 3. Golang plots for the vacuum-outlet GC system. (a) Golang plot for 3-octanone ($k = 9.5$), (b) Golang plot for 2-pentanone ($k = 0.7$). Experimental: isothermal separation at 36°C ; make-up gas was used to minimize extra-column band broadening in the detector; $n = 3$ for each point.

0.30–0.45 atm) as optimum. However, the range of plate height values in Fig. 3 is relatively small and the use of faster average carrier gas velocities than optimal results in substantial reductions in analysis time with only a relatively small loss in efficiency. As can be seen in chromatograms (b) and (c) in Fig. 2, the loss in component-pair resolution with $p_o = 0.25$ atm is small relative to a p_o value of 0.7 atm, but a decrease of about two times in the analysis time is obtained. Figure 4 shows the chromatogram of a 16-component test mixture obtained with a p_o value of 0.25 atm. The initial column temperature was 30°C , and a 10°C ramp to 60°C was initiated 1.0 min after the injection.

3.2 Peak area linearity with sample mass and repeatability

The sample recovery performance of the multibed trap as a function of the mass of analyte challenging the trap was evaluated. A mixture containing some of the compounds indicated in Table 1 was used to obtain plots of log peak area *versus* log sample collection time for both wet and dry samples. Sampling collection time was varied to cover a three orders of magnitude mass dynamic range for each compound (from 0.06 to 6.1 μg , which are

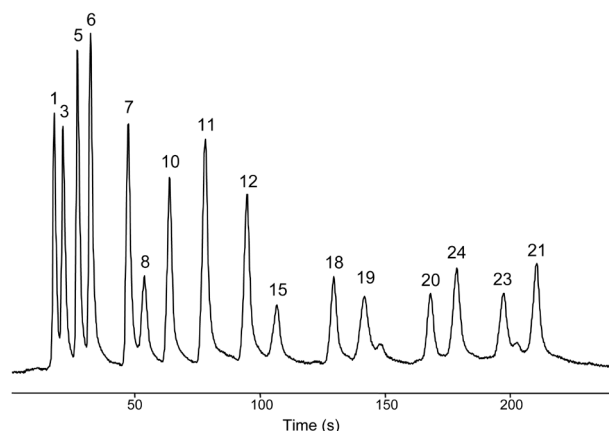


Figure 4. Chromatogram of a 16-component synthetic mixture. Experimental: $p_0 = 0.25$ atm, no make-up gas, temperature program: 60 s at 30°C, 10°C/min to 60°C. Peak numbers correspond to the compound numbers in Table 1.

similar and larger amounts than expected in industrial, environmental, and indoor and outdoor air samples). Statistical data obtained for the plots are shown in Table 1. Three replicate experiments were conducted at each sampling time, and six different sampling times were used for each calibration. The slopes of log–log plots for all the compounds were in the range 0.96–1.09 for dry samples and 0.97–1.06 for humid samples, indicating an adequate peak-area correlation with the mass of analyte introduced in the system. The evaluation of the residuals of the calibration curves showed that all the compounds had a linear response in the range and conditions evaluated. These results indicate that there was no sample breakthrough of the compounds in the conditions evaluated, which suggests that no breakthrough is expected in the analysis of air samples, except in the case of periods of heavy contamination. Previous studies [40, 41] have demonstrated that the combination of carbon-based sorbents used in the multi-bed trap (three graphitized carbons and one carbon molecular sieve) only results in an appreciable effect of the water vapor content of the samples on the collection/desorption efficiency of the most polar and volatile alcohols (*e.g.* methanol), which cannot be analyzed with the PID. These compounds are mainly retained by the carbon molecular sieve bed (Carboxen 1000).

Run to run repeatability was determined for the 29 compounds evaluated in this study. The determination of the peak area repeatability yielded $RSD \leq 2\%$ ($n = 3$) for all the compounds and concentrations tested. $RSD \leq 1\%$ ($n = 3$) were obtained when the repeatability in the retention times was evaluated for sample replicates of the same concentration. RSD values were slightly larger ($\leq 4\%$ for the less retained compounds and $\leq 8\%$ for the more retained) when sample replicates of different concentrations were evaluated. This is due to the variation

in the time at the peak maximum at increased amounts of analyte introduced in the system. If the time at the beginning of the peak was computed instead of the time at the peak maximum, RSD s were always $\leq 1\%$.

3.3 Sample decomposition

Sample decomposition of airborne VOCs during collection, transport, and injection into the GC is an important issue. The system evaluated here uses an online sorption trap, which allows for immediate analyte injection into the GC column after sample collection is complete. This eliminates the risk of sample loss and decomposition during transport and storage. However, an important problem in the use of the sorbent-trap technique is the relatively high temperatures required for the complete and rapid desorption of the trapped compounds, which can lead to thermal decomposition of some analytes [41]. This thermal decomposition is the result of an oxidation process and the percentage of degradation of the compounds is affected by the carrier gas circulating through the surface of the sorbents during the thermal desorption step. Those VOCs that can be oxidized showed larger percentages of decomposition when air was used as the carrier gas than with hydrogen.

The use of vacuum-outlet ambient air as the carrier gas in this study limits the use of high desorption temperatures. This results in an increased extra-column band broadening because the injection plug width increases when the desorption pulse decreases [40]. Figure 5 shows the chromatograms obtained in the analysis of a sample containing γ -terpinene, a terpene compound that was found to be highly reactive during its desorption from carbon-based sorbents at elevated temperatures [41]. A small decomposition peak is observed at a retention time of 171.1 s with a desorption pulse of 200°C (Fig. 5a). The peak area corresponding to the target compound ($t_R = 192.0$ s) decreased with the temperature applied during the heating pulse (from 200 to 380°C) whereas the peak corresponding to the decomposition product increased. Similar behavior has been observed for all the terpenes evaluated (Table 1). All ketones and aldehydes evaluated, except benzaldehyde, also showed some decomposition but this started at desorption temperatures of $\sim 250^\circ\text{C}$. Those compounds marked as “No” in the last column of Table 1 did not show decomposition during desorption at heating pulses up to 380°C.

The determination of biogenic VOCs are of great interest in the analysis of outdoor and indoor air because large quantities of reactive compounds, including terpenes and oxygen-containing terpene structures, are emitted into the atmosphere by vegetation [42–44]. Moreover, terpene concentrations in the atmosphere are also increasing due to the increased use of natural products such as terpene-based cleaning solvents, fragrances

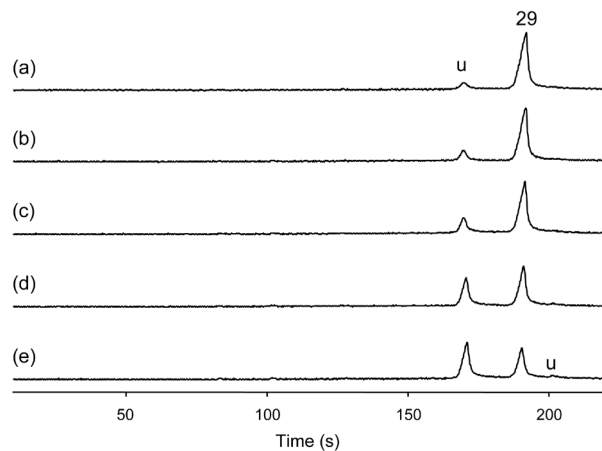


Figure 5. Chromatograms obtained in the analysis of a sample containing γ -terpinene at different temperature pulses for the desorption step. (a) 200, (b) 250, (c) 300, (d) 350, and (e) 380°C. Analysis conditions are the same as in Fig. 4. Key: 29, γ -terpinene; u, unknown.

and wooden furniture [45]. Thus, the results obtained in this study indicate that desorption pulses lower than 200°C are recommended for the analysis of environmental air containing highly reactive compounds with the system developed.

3.4 Applications

The system described in this study has been tested for different applications in order to explore its features and capabilities. Figure 6 shows the headspace analysis of an essential oil (Spruce, black) at different sampling times. The number of peaks that can be observed for this sample is smaller than those obtained by using an FID as the detector [41] because of the use of a PID in this study. An 80 s sampling time (Fig. 6d) results in an increased sensitivity but a lower resolution for the main components due to the extra-column band broadening.

In Fig. 7, chromatograms obtained in the analysis of breath samples (720 mL expired breath) from two nonsmoking volunteers are shown. The need to apply temperatures of <200°C during the desorption pulse yields a broad peak at the beginning of the chromatogram corresponding to the coelution of acetone and isoprene, the main components in human breath samples [46]. These two compounds cannot be separated with the 10-m DB-5 column used in this study. Figure 7a corresponds to the breath of a volunteer after taking a flavored lozenge. The peak at 209.1 s corresponds to limonene, a common terpene that may be a flavor/fragrance additive in the lozenge. Trace amounts of benzene ($t_R = 31.1$ s) and toluene ($t_R = 46.7$ s) were also detected in this sample. All other peaks detected correspond to unknown compounds. Figure 7b was obtained from a volunteer more

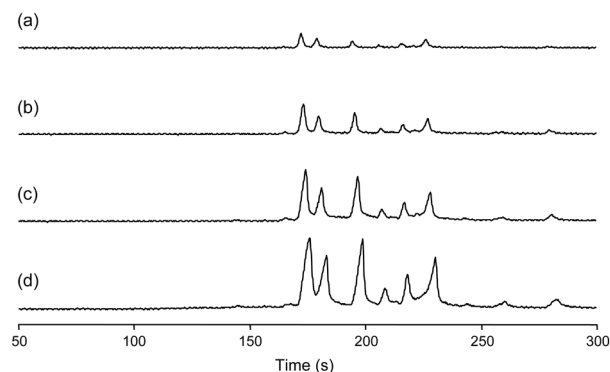


Figure 6. Chromatograms obtained in the analysis of an essential oil (Spruce, black). Sampling times of (a) 10, (b) 20, (c) 40, and (d) 80 s were used. Experimental conditions: $p_o = 0.25$ atm; no make-up gas; temperature program: 60 s at 30°C, 15°C/min to 85°C and hold for 60 s; 1 μ L of the standard injected into a 10 L sampling bag.

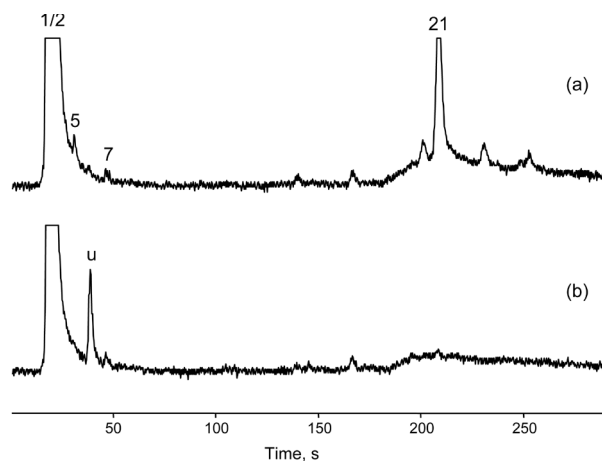


Figure 7. Chromatograms obtained in the analysis of breath samples from two nonsmoking volunteers (a) after taking a flavored lozenge and (b) after more than 2 h without eating or drinking. Experimental conditions: $p_o = 0.25$ atm; no make-up gas; temperature program: 60 s at 30°C, 10°C/min to 75°C; 720 mL expired breath (10 min sampling at 72 mL/min from a sample collected in a 10 L Tedlar sampling bag). Peak numbers correspond to the compound numbers in Table 1 (u: unknown).

than 2 h after taking any food or beverage. Benzene and limonene were not detected in this sample. An unknown component was detected at a retention time of 40.0 s. As can be seen in Fig. 7, the pattern for the two chromatograms differs but it is already known that breath samples vary widely in their composition [46, 47].

The last application tested with the system developed was the analysis of environmental air. Figure 8 shows the analysis of our laboratory air on three different working days. Contamination due to acetone, a common solvent used in the laboratory, and some unknown compounds were present each day at varying levels.

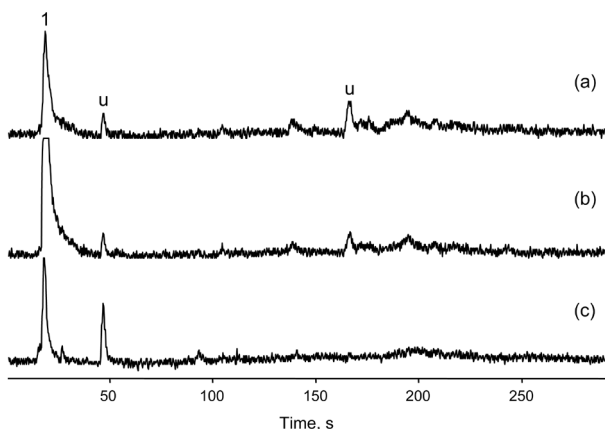


Figure 8. Analysis of indoor air. Chromatograms obtained for the analysis of our laboratory air on three different days. Experimental conditions are same as in Fig. 7. Key: 1, acetone; u, unknown.

4 Concluding remarks

A combination of a multi-stage preconcentrator, at-column heating and PID detector has been found to produce satisfactory results in this preliminary study devoted to the design of a portable GC system for on-site monitoring of large-volume atmospheric samples. The main advantage of the system is its use of vacuum-outlet atmospheric air as the carrier gas reducing the need for compressed gas tanks, an important problem with other portable instruments. One of the drawbacks of the use of atmospheric air is rapid stationary phase decomposition at elevated temperatures. However, this problem can be solved by limiting the upper temperatures applied to the column during the separation stage. This will result in broader peaks and loss of efficiency of the system. However, it will ensure the detected compounds are actually present in the sample and will prevent the false detection of compounds coming from the decomposition of the target analytes. Another disadvantage is that using PID as a detector limits the number of compounds that can be detected. This can be solved by using mass-sensitive transducers such as thickness-shear mode resonator (TSMR) and surface acoustic wave (SAW) devices.

The sample recovery of the sorbent trap has been found to be adequate to avoid breakthrough of VOCs in air samples with light contamination. Some breakthrough may appear in periods of heavy contamination. However, it is expected that a portable instrument for on-site analyses will be used to detect early stages of air contamination and to act before the apparition of periods of heavy contamination.

The main problem associated with the use of vacuum-outlet atmospheric air system is the need to use a low temperature pulse during the desorption step of the retained VOCs from the carbon-based sorbents. However,

a portable GC device is intended for screening analysis and the loss of resolution is largely overcome by the reduction of consumables and the increased portability of the resulting instrument. Future work is necessary to obtain a miniaturized and portable instrument. However, this preliminary study shows promising results and demonstrates that the use of instruments using vacuum-outlet atmospheric air can be a good choice for this purpose.

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5 References

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