



Microfabricated ionic liquid column for separations in dry air

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ARTICLE INFO

Article history:

Received 4 January 2020

Revised 25 February 2020

Accepted 26 February 2020

Available online 27 February 2020

Keywords:

Gas chromatography

Ionic liquid

Stationary phase

Dry air

Microfabricated column

ABSTRACT

Micro gas chromatography (μ GC) is a technique developed for rapid, *in situ* analysis of volatile organic compounds (VOCs) for environmental protection, industrial monitoring, and toxicology. While reduced μ GC size and power requirements allow for increased portability, the low moisture and oxygen resilience of current microcolumn technology result in increased peak broadening and tailing for humid samples, which necessitates the use of bulky helium or nitrogen carrier gas cartridges. Developing a microcolumn to address these deficiencies is desirable to improve μ GC field performance and further reduce μ GC system size. This paper reports the development and characterization of a microfabricated phosphonium ionic liquid (μ IL) column and demonstrates separation of both polar and nonpolar compounds using this column via analyses of alcohols, chloroalkanes, aromatics, aldehydes, fatty acid methyl esters, and alkanes. The μ IL column achieved operation at temperatures up to 345 °C for fatty acid methyl ester and alkane separation. Notably, all separations in this study used dry air as the carrier gas, showing that analysis of a diverse range of compounds was possible in the presence of oxygen. After exposure to dry air for 48 h at temperatures up to 220 °C, the μ IL column's peak capacity was only degraded by 8.92%, which validated its long-term robustness against oxygen. The column's separation performance was not degraded by high moisture concentrations or long-term moisture exposure, also manifesting its robustness to moisture. The high temperature, moisture, and oxygen resilience of the μ IL column enable more rapid separations in varying field environments without requiring additional μ GC accessories (e.g., humidity filters and carrier gas cartridges). The μ IL column is therefore expected to be useful for integration into future μ GC devices.

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Micro gas chromatography (μ GC) is a separation technique targeted at field analysis of volatile organic compounds (VOCs). Miniaturization of individual GC components (*i.e.*, injectors, columns, detectors) allows for reduction of μ GC system size and power requirements, enabling on-site, rapid, real-time analysis of VOCs [1–15] for environmental and industrial monitoring and pollution and toxicology analysis. Enhancement of individual microcomponent performance, especially microcolumn characteristics, allows for reinforcing these strengths and improving μ GC separation robustness [1,3,4,6,10]. For example, integration of these microcolumns with heaters and other micro-components has successfully minimized dead volume and enabled rapid, highly uniform column heating [1–3,5,7,9,11,13,16–18]. However, most current μ GC stationary phase coating materials have low oxygen and moisture robustness, which leads to separation performance degradation

with increased peak broadening and tailing [19]. These traits necessitate the use of bulky helium or nitrogen carrier gas cartridges and result in relatively large and heavy μ GC systems. This increased size and weight are less suitable for field applications (especially those that require long-term unmanned operation). Previous studies have demonstrated systems using a carrier gas of ambient air [18–27]. However, these systems only permitted a limited selection of column coating materials and temperature ranges (sometimes up to 150–200 °C [18,20,23–26], but not above this range especially for extended periods), which prohibits the general-purpose use of these systems in vapor sensing of a greater range of volatile compounds. Thus, in order to improve μ GC portability and performance, it is necessary to develop microcolumns utilizing stationary phases capable of withstanding high moisture and oxygen exposure. Such stationary phases will allow for a broader range of VOC analysis using fewer μ GC accessory components.

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Previous work has demonstrated the versatile use of ionic liquids (IL) in GC separations, most notably as highly tunable compounds with unique separation capabilities [28–52]. By modifying the structure of the cation or anion, ILs can be tuned for separation of fatty acid methyl esters (FAMES) [35,40,49,52–56], chiral compounds [38,45,51], nonpolar analytes [37,38,57], or aromatics and fragrances [28,30,34,36,43,44,47,52]. Some ILs also exhibit affinities to both dipolar and nonpolar solutes [30,41,45], allowing for separation of analytes of varying polarities with a single column. While the flexibility of different ILs is useful for development of highly tailored microcolumns, their moisture [33,38,41,44,48,51,58–61] and oxygen [29,30,44,46,50] resilience (or, ability to separate moisture and compounds containing oxygen – especially reactive oxygens such as formaldehyde), additionally, are greatly beneficial for microcolumns in portable GC systems. Many other column coatings are adversely impacted by moisture in samples and may require some form of moisture filtration; reactivity with oxygen at higher temperatures also necessitates the use of N₂, He, or H₂ carrier gas cartridges. By utilizing a suitable IL film instead, it becomes possible to develop a μ GC device for which these accessories are no longer necessary, thus reducing the system's size and weight. Furthermore, the high-temperature resilience of many ILs [28,30,32,38,43,48,62–64] allows for more rapid separation of heavier compounds and therefore faster μ GC analysis times. Some tradeoffs for eliminating the carrier gas cartridge may include addition of hydrocarbon filters, moisture filters for some systems (e.g. to maintain preconcentrator cleanliness rather than only prevent IL degradation), and particulate filters. These, however, can be inserted as inline fluidic or even microfluidic components, allowing them to be much smaller than the comparatively large carrier gas cartridge.

This paper reports the design, fabrication, and evaluation of a wall coated open tubular microfluidic phosphonium ionic liquid (μ IL) column. Fabrication and column coating procedures are detailed herein, and six separations, i.e., separation of alcohols, chloroalkanes, aldehydes, aromatics, alkanes, and FAMES, manifest the ionic liquid column's ability to separate both polar and non-polar compounds of varying volatilities using dry air as the carrier gas. Moisture and oxygen robustness characterized in the presence of dry air also show little to no column degradation due to moisture and slow degradation by oxygen at high temperatures. By showing the ability to separate a wide variety of compounds using a carrier gas of dry air, the μ IL column demonstrates applicability to a wide range of μ GC applications (e.g., 2D μ GC or ultra-compact portable GC) by alleviating the need for auxiliary carrier gas cartridges through its high oxygen resilience. The μ IL column is therefore expected to be useful for integration into future field and environmental μ GC devices.

1. Experimental

1.1. Materials

All reagents used in this study were purchased from Sigma-Aldrich (St. Louis, MO) and Restek (Bellefonte, PA). Benchmark reagents (analytical standard grade): methanol, ethanol, propanol, butanol, pentanol, formaldehyde solution, acetaldehyde, propionaldehyde, butyraldehyde, benzaldehyde, 1-chlorobutane, 1-chloropentane, 1-chlorohexane, 1-chloroheptane, 1-chlorooctane, 1-chlorododecane, benzene, toluene, styrene, ethylbenzene, o-xylene, 1,2-dichlorobenzene, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane, tetradecane, *n*-Paraffin mix C₁₈, C₂₀, C₂₂, C₂₄ (P/N 47108, Sigma Aldrich), FAME #7 Mix (P/N 35016, Restek), FAME #8 Mix (P/N 35017, Restek), methyl caproate. Coating reagents: trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)amide, ammonium hydroxide, hydrogen

peroxide, sodium chloride tablets, dichloromethane. Hysol® 1C™ Epoxy was purchased from Ellsworth Adhesive (Germantown, WI). Polyimide sealing resin (P/N 23817) for the connection interface was purchased from Sigma-Aldrich (St. Louis, MO). Deactivated fused silica tubing (P/N 10010) with 250 μ m inner diameter was purchased from Restek. N-type silicon wafers (P/N 1095, 100 mm diameter, 500 μ m thickness) and Borofloat 33 glass (P/N 517) were purchased from University Wafer. All materials were used as purchased without further purification or modification. The microcolumn was evaluated on all separations using an Agilent 6890 benchtop GC equipped with a flame ionization detector (FID). Dry air was used as the carrier gas.

1.2. Microcolumn coating

Microcolumns were fabricated via plasma etching on silicon wafers, as reported previously (see Fig. S1) [65]. The microcolumn had a cross section of 160 μ m x 160 μ m and a total length of 5 m. The microcolumn was coated based on a procedure adapted from previous research [30,32,66]. Prior to coating, the column was silanized by eight repeated injections of liquid hexamethyldisilazane under a 0.5 mL/min flow of helium at a temperature of 90 °C. Following silanization, the column was washed sequentially with dichloromethane, water, and acetone. A solution of ammonium hydrogen peroxide (APM) was prepared from a mixture of 10 mL of deionized water, 0.1 mL of H₂O₂ solution (30% w/w in aqueous solution), and 0.1 mL of NH₄OH (28–30% NH₃ w/w). 100 μ L of the APM mixture was flowed through the column at a flow rate of 20 cm/min in order to roughen the silicon surface [67]. The column was then washed with acetone. Subsequently, a saturated solution of sodium chloride in dichloromethane was prepared at room temperature, sonicated, then diluted by adding 1 mL of solution to 5 mL of dichloromethane (and sonicated again) [66]. The column was filled with solution, allowed to stand for 2 h, then emptied with dry air at a flow velocity of 5 cm/min.

400 mg of trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)amide was added to 2 mL of diluted sodium chloride in dichloromethane (see above). The column was dynamically coated by filling with 300 μ L of solution, then pushing the liquid out at a rate of 1 cm/min (approx. 5 psi pressure, see Figure S1(C)). A dummy column was attached to the end of the column during this process in order to maintain a constant flow resistance. The column was subsequently purged with dry air and dried under a helium flow of 0.3 mL/min at 100 °C for 2 h. The column was then aged at 200 °C for another 2 h. A photo of the coated column is provided in Figure S1(D). A second column was coated using the same procedure, but using a further diluted sodium chloride solution for salt deposition (1 mL–8 mL of dichloromethane) and a diluted ionic liquid solution (200 mg of ionic liquid added to 2 mL of solution) to demonstrate the capability for coating columns with different retention characteristics. The second column was used for moisture and dry air stress testing analysis (see Oxygen and moisture robustness).

1.3. Experimental setup

The μ IL column was evaluated on all separations in an Agilent 6890 benchtop GC equipped with an injection port and a flame ionization detector (FID). Manual injections were made and the injection port was set to splitless unless otherwise stated. Temperature ramping was controlled by the GC oven. Dry air was used as the carrier gas.

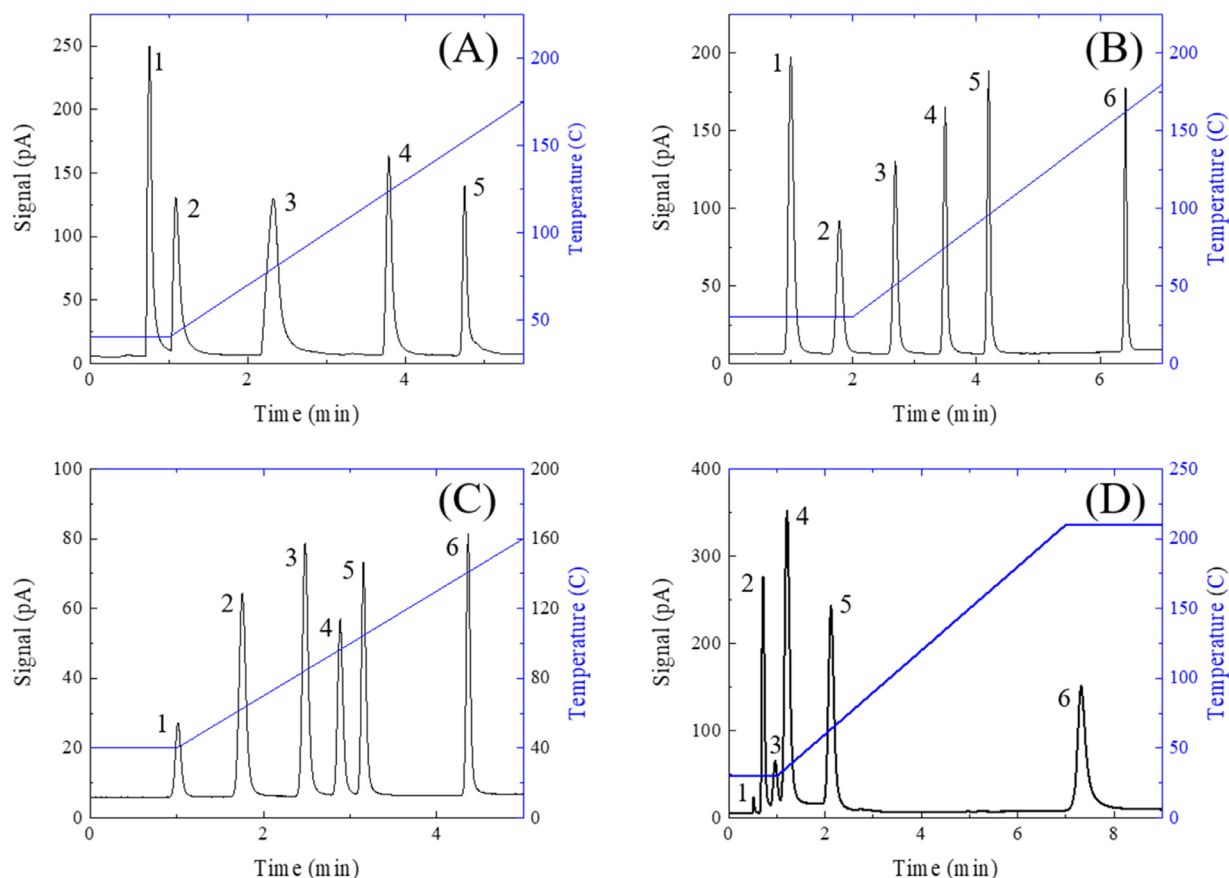


Fig. 1. Separation of alcohols (A), chloroalkanes (B), aromatics (C), and aldehydes (D). Splitless injections of 0.04 μL of mixture liquids were made. Carrier gas flow rates: 2 mL/min at each initial temperature. Compound lists, elution orders, retention times, and full widths at half maxima (FWHMs) are provided in Table 1.

2. Results and discussion

2.1. Separation of alcohols, chloroalkanes, aromatics, and aldehydes

This benchmarking experiment presents analysis of alcohols, chloroalkanes, aromatics, and aldehydes, *i.e.* separation of various groups of polar compounds. The following temperature ramping profiles were used: 30 $^{\circ}\text{C}$ (held for 1 min) to 190 $^{\circ}\text{C}$, 40 $^{\circ}\text{C}$ (held for 2 min) to 190 $^{\circ}\text{C}$, 50 $^{\circ}\text{C}$ (held for 1 min) to 170 $^{\circ}\text{C}$, and 30 $^{\circ}\text{C}$ (held for 1 min) to 210 $^{\circ}\text{C}$ for alcohols, chloroalkanes, aromatics, and aldehydes, respectively. All temperature ramping rates were set to 30 $^{\circ}\text{C}/\text{min}$ and all flow rates were 2 mL/min (measured at each initial temperature). Resulting chromatograms are presented in Fig. 1. All analytes are clearly separated by the μL column, with retention times and full widths at half maxima (FWHMs) reported in Table 1. Golay plots for methanol and chlorobutane at 80 $^{\circ}\text{C}$ (isothermal) were generated (Fig. 2) and optimized height equivalents to theoretical plates (HETPs) of 0.87 mm ($k = 1.21$ at 15 cm/s) and 0.95 mm ($k = 1.42$ at 7 cm/s) were obtained for methanol and chlorobutane, respectively, representing 1147 and 1051 plates per meter.

2.2. Separation of fatty acid methyl esters and alkanes

Trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)amide columns have previously shown to offer efficient separation of fatty acid methyl esters (FAMES) [35,40,49,52,53,55,56], which is useful for characterization of fats and oils in food. The following experiment (Fig. 3) demonstrates the μL column's ability to separate FAMES from C6:00 to C15:00 with temperature

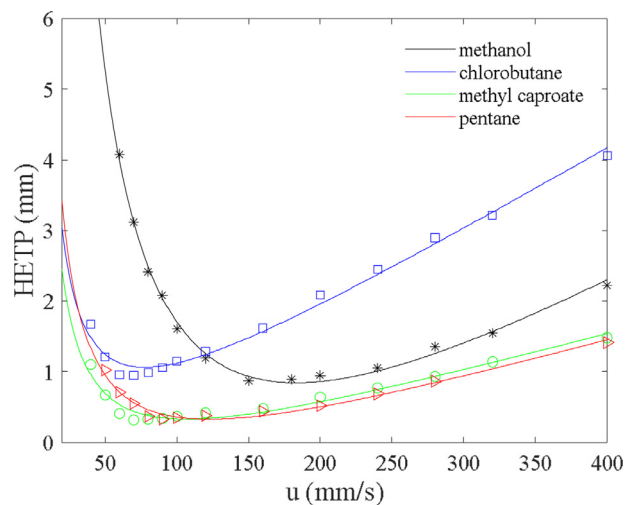


Fig. 2. Golay plots for methanol, chlorobutane, methyl caproate, and pentane. The temperature was set to 80 $^{\circ}\text{C}$ for methanol and chlorobutane, 160 $^{\circ}\text{C}$ for methyl caproate, and 60 $^{\circ}\text{C}$ for pentane (isothermal at each temperature). Optimized HETPs: methanol – 0.87 mm; chlorobutane – 0.95 mm; methyl caproate – 0.32 mm; pentane – 0.33 mm.

ramping from 120 $^{\circ}\text{C}$ to 345 $^{\circ}\text{C}$ at 30 $^{\circ}\text{C}$ per min. The carrier gas flow rate was set to 2 mL/min at 120 $^{\circ}\text{C}$. All FAMES were fully separated, with retention times and FWHMs provided in Table 2. The average baseline signal varied from 5.51 pA (measured from 0.01 to 0.5 min) to 24.72 pA (measured from 7.2 to 7.5 min). A Golay plot for methyl caproate (C6:00) was obtained at 160 $^{\circ}\text{C}$

Table 1

Retention times (RTs) and FWHMs of μ L separation of alcohols (A), chloroalkanes (B), aromatics (C), and aldehydes (D). Analytes are provided in order of elution for each separation. All values are provided in minutes.

(A)	RT	FWHM	(B)	RT	FWHM
(1) Methanol	0.754	0.0677	(1) Chlorobutane	1.000	0.1060
(2) Ethanol	1.088	0.0955	(2) Chloropentane	1.787	0.1220
(3) Propanol	2.324	0.1820	(3) Chlorohexane	2.690	0.0895
(4) Butanol	3.791	0.0890	(4) Chloroheptane	3.495	0.0703
(5) Pentanol	4.755	0.0648	(5) Chlorooctane	4.198	0.0612
			(6) Chlorododecane	6.407	0.0523
(C)	RT	FWHM	(D)	RT	FWHM
(1) Benzene	1.011	0.0835	(1) Formaldehyde	0.514	0.0328
(2) Toluene	1.755	0.0987	(2) Acetaldehyde	0.710	0.0685
(3) Styrene	2.478	0.0837	(3) Methanol	0.962	0.1032
(4) Ethylbenzene	2.885	0.0787	(4) Propionaldehyde	1.210	0.1298
(5) o-Xylene	3.152	0.0658	(5) Butyraldehyde	2.123	0.1452
(6) 1,2-dichlorobenzene	4.360	0.0573	(6) Benzaldehyde	7.320	0.2145

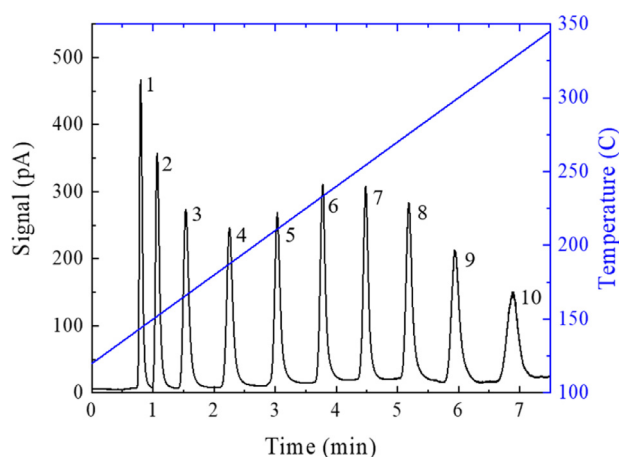


Fig. 3. Separation fatty acid methyl esters. A splitless injection of 0.1 μ L mixture liquid was made using a carrier gas flow rate of 2 mL/min at 120 °C. 1. C6:00; 2. C7:00; 3. C8:00; 4. C9:00; 5. C10:00; 6. C11:00; 7. C12:00; 8. C13:00; 9. C14:00; 10. C15:00. Analysis is provided in Table 2.

Table 2

Retention times (RTs) and FWHMs of μ L column separation of FAMES. All values are provided in minutes.

	RT	FWHM
(1) C6:00	0.797	0.0607
(2) C7:00	1.069	0.0809
(3) C8:00	1.536	0.1127
(4) C9:00	2.251	0.1159
(5) C10:00	3.033	0.1116
(6) C11:00	3.777	0.1058
(7) C12:00	4.477	0.1030
(8) C13:00	5.184	0.1213
(9) C14:00	5.936	0.1610
(10) C15:00	6.880	0.2270

(isothermal, Fig. 2) and an optimized HETP of 0.32 mm ($k = 1.32$ at 7 cm/s) was achieved, representing 3132 plates per meter.

Analysis of alkanes ranging from C_5 to C_{24} was also performed, demonstrating the μ L column's ability to separate nonpolar analytes as well (note that FAMES are also relatively nonpolar compared to the groups of analytes listed in the previous section). Fig. 4 demonstrates separation of these alkanes using a temperature ramping profile from 50 °C (held for 0.5 min) to 345 °C at 45 °C per min. The carrier gas flow rate was set to 3 mL/min at 50 °C. Again, all alkanes were fully separated, with C_5 and C_6 no-

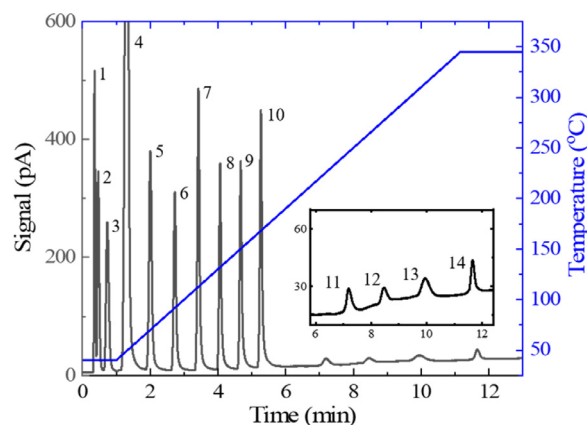


Fig. 4. Separation C_5 – C_{24} alkanes. A splitless injection of 0.1 μ L mixture liquid was made using a carrier gas flow rate of 3 mL/min at 50 °C. 1. Pentane; 2. Hexane; 3. Heptane; 4. Octane; 5. Nonane; 6. Decane; 7. Undecane; 8. Dodecane; 9. Tridecane; 10. Tetradecane; 11. Octadecane; 12. Eicosane; 13. Docosane; 14. Tetracosane. The inset provides a zoom-in of the octadecane, eicosane, docosane, and tetracosane peaks. Analysis is provided in Table 3.

Table 3

Retention times (RTs) and FWHMs of μ L separation of C_5 – C_{24} alkanes. All values are provided in minutes.

	RT	FWHM
(1) C_5	0.357	0.0422
(2) C_6	0.465	0.0652
(3) C_7	0.733	0.1015
(4) C_8	1.313	0.1145
(5) C_9	2.002	0.0998
(6) C_{10}	2.729	0.0872
(7) C_{11}	3.427	0.0805
(8) C_{12}	4.066	0.0765
(9) C_{13}	4.674	0.0768
(10) C_{14}	5.272	0.0783
(11) C_{18}	7.191	0.2065
(12) C_{20}	8.473	0.2148
(13) C_{22}	9.963	0.3348
(14) C_{24}	11.652	0.1587

tably separated at 50 °C. Retention times and FWHMs are provided in Table 3. An optimized HETP of 0.33 mm ($k = 0.68$ at 9 cm/s) was obtained for pentane at 60 °C (isothermal, Fig. 2), representing 3055 plates per meter. The average baseline signal varied from 5.63 pA (measured from 0.01 to 0.5 min) to 28.2 pA (measured from 12 to 12.6 min). Together with the baseline bleeding mea-

Table 4

Peak capacities calculated for C₈–C₁₄ alkanes after 16, 32, and 48 h of exposure to dry air. Peak capacities are calculated by summing all resolutions between adjacent peaks (i.e., summing resolutions between C₈/C₉, C₉/C₁₀, ..., C₁₃/C₁₄). Peak capacity decreases with increased exposure to dry air, degrading by 8.92% at 48 h.

	Peak capacity
Initial	18.05
At 16 h	17.92
At 32 h	17.23
At 48 h	16.44

sured from the FAMES separation, the μ L column's low bleed at 345 °C suggests that the column is stable at high temperatures for at least short periods, enabling rapid analysis of heavier compounds.

2.3. Oxygen and moisture robustness

The μ L column's robustness to oxygen was tested by conditioning in dry air under elevated temperatures. Dry air was flowed through the column for 3 periods of 16 h at 180 °C, 200 °C, and 220 °C for a total of 48 h of conditioning. The flow rate was set to 0.5 mL/min at each temperature. Degradation in performance was analyzed on C₈ to C₁₄ alkanes using a temperature profile of 40 °C (held for 1 min) to 190 °C at a temperature ramping rate of 30 °C/min with a flow rate of 2 mL/min measured at 40 °C. Chromatograms for the initial separation, after 16 h (at 180 °C), after 32 h (i.e., 16 h of 200 °C after the prior 16 h), and after 48 h (i.e., 16 h of 220 °C after the prior 32 h) are provided in Fig. 5 (note that a mixture of C₅–C₁₄ was used, but since C₅–C₇ were not well separated, only C₈–C₁₄ were analyzed). Retention times and FWHMs were both gradually reduced with continuous conditioning and could not be directly compared to the original separation. Instead, resolutions between adjacent peaks (e.g., between C₈ and C₉) were calculated using the following formula:

$$R = 1.18 \times \frac{t_2 - t_1}{w_1 + w_2}$$

where t_1 and t_2 are the retention times of the first and second peaks, respectively. w_1 and w_2 are the FWHMs of the first and second peaks, respectively.

A summation over all resolutions from C₈ to C₁₄ (i.e., $R_{C_8/C_9} + R_{C_9/C_{10}} + \dots + R_{C_{13}/C_{14}}$) yielded the peak capacity for each chromatogram (averaged over 5 runs). A gradual decrease in peak capacity was observed, from 18.05 prior to conditioning to 16.44 post-conditioning, a decrease of 8.92% after 48 h of exposure to dry air at elevated temperatures. In comparison, the peak capacity of a microfabricated OV-5-coated column was found to degrade from 37.28 to 30.32 after 16 h of exposure to dry air at 200 °C, representing an 18.67% decrease in performance (see Table S1). When

Table 6

Peak capacities calculated for C₁₀–C₁₄ alkanes for dry injections (control), with 500 μ L of added water vapor, 1 μ L of added liquid water, after 50 injections of liquid water, and after 100 injections of liquid water. Peak capacities are calculated by summing all resolutions between adjacent peaks. p -values are calculated from 5 runs for each set of injections and significance is taken at $p = 0.05$. No significant differences in peak capacity were observed for either moisture injection or after stress testing.

	Peak capacity	p -value
Dry	7.783	–
Vapor	7.871	0.498
Liquid	7.842	0.788
50 injections	7.915	0.342
100 injections	8.037	0.086

considering the maximum temperature used for this alkanes separation (up to C₁₄), the column spends no more than 2 min above 180 °C on each run; therefore, the 48 h of conditioning represents at least ~1500 runs with only a 8.92% reduction in performance. This low degradation rate demonstrates the μ L column's high robustness to oxygen in dry air, allowing for operation using a dry air carrier gas even over extended periods. Notably, the lifetime of at least 48 h of operation at elevated temperatures is expected to be more than sufficient for most portable GC applications.

Finally, for field applications, a separation column's performance in the presence of moisture is of concern, especially for samples containing water and solvents. While moisture can affect retention times and result in peak tailing and broadening (for normal columns such as OV-1 or OV-5 columns), ionic liquids have previously been shown to provide reasonable moisture resilience and the capacity to separate water [33,38,41,44,48,51,58,59]. To verify this, C₁₀ to C₁₄ alkanes were injected with and without added moisture (added concurrently into the syringe containing the alkane sample) using a temperature ramping profile of 100 °C (held for 0.5 min) to 220 °C at 60 °C/min with a flow rate of 1.2 mL/min (measured at 100 °C). 0.025 μ L injections were made with no moisture, with 500 μ L of water vapor (heated to 80 °C to increase the partial pressure in headspace), and with 1 μ L of added liquid water (5 repetitions for each case). Sample chromatograms are provided in Fig. 6. Comparisons between retention times and FWHMs between dry injections and injections with moisture are made using paired Student's t -tests and converting resulting T -scores to p -values. These retention times, FWHMs, and p -values are provided in Table 5. Peak capacities are provided in Table 6. As shown in Table 5, the only two significant differences were observed for FWHMs for C₁₀ and C₁₁ with liquid water injection. FWHM broadenings of 19% and 10% were observed for C₁₀ and C₁₁, respectively. However, the overall peak capacity was unaffected (Table 6), suggesting that the overall column

Table 5

Retention times (RTs), FWHMs, and p -values of C₁₀–C₁₄ alkanes with no added moisture, 500 μ L of added water vapor, and 1 μ L of added liquid water. The water vapor was heated to 80 °C prior to injection in order to increase the partial pressure in headspace. RTs and FWHMs are provided in minutes. All values are calculated based on 5 runs. p -values were obtained by comparing moisture separations with dry separations, with significance taken at $p = 0.05$. p -values are provided as RT/FWHM; the only two significant values were for FWHMs for C₁₀ and C₁₁ with liquid water injection. FWHM broadenings of 19% and 10% were observed for C₁₀ and C₁₁, respectively. No broadening was observed for vapor injection.

	RT (Dry)	FWHM (Dry)	RT (vapor)	FWHM (vapor)	p -value (vapor)	RT (liquid)	FWHM (liquid)	p -value (liquid)
C ₁₀	0.737	0.0890	0.726	0.0921	0.309/0.468	0.724	0.1058	0.532/0.005
C ₁₁	1.000	0.1162	0.999	0.1151	0.966/0.507	1.019	0.1279	0.436/0.033
C ₁₂	1.372	0.1196	1.379	0.1193	0.746/0.875	1.411	0.1191	0.297/0.912
C ₁₃	1.777	0.1053	1.770	0.1044	0.730/0.765	1.807	0.1008	0.281/0.304
C ₁₄	2.158	0.0921	2.156	0.0910	0.905/0.649	2.182	0.0881	0.270/0.169

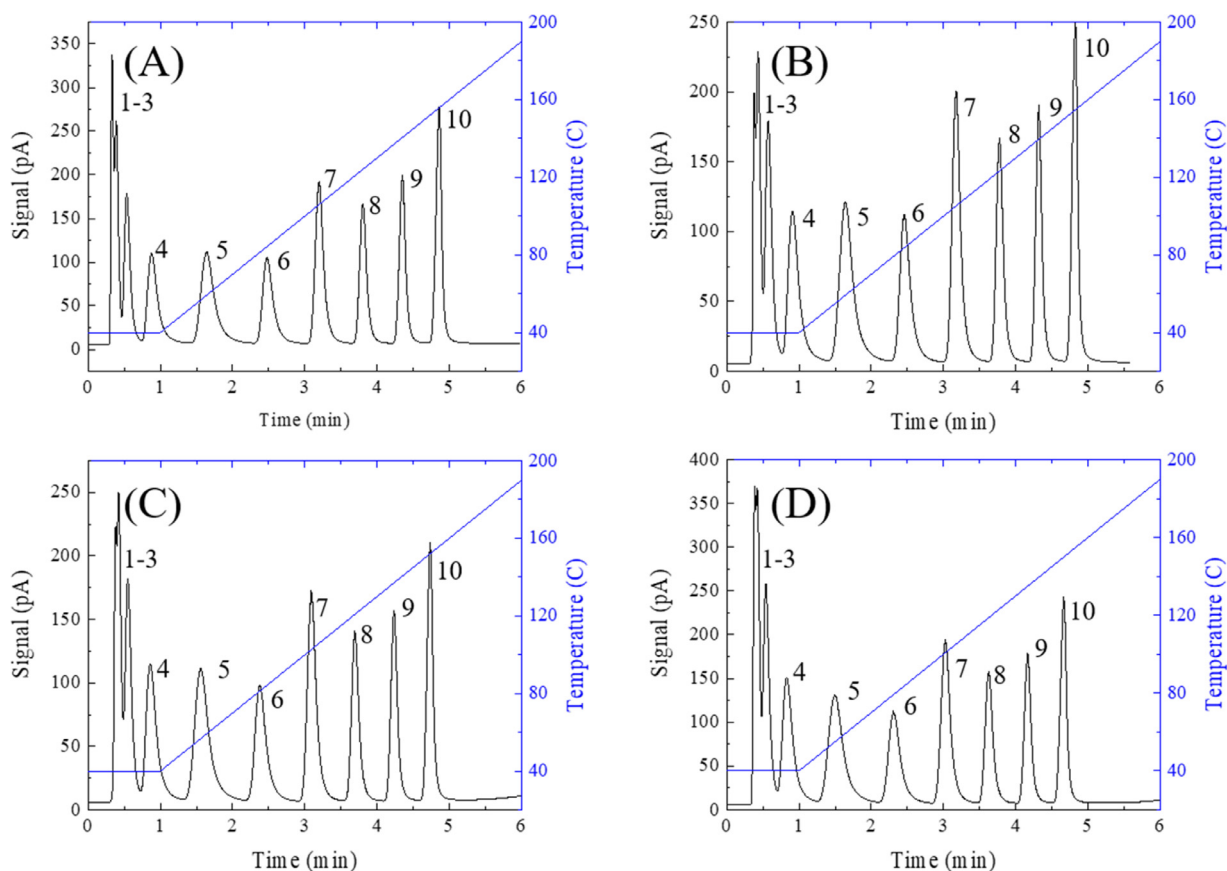


Fig. 5. Separation of C_5 – C_{14} alkanes prior to conditioning (A), after 16 h (B), after 32 h (C), and after 48 h (D). Splitless injections of 0.04 μ L of mixture liquids were made. Carrier gas flow rate: 2 mL/min at 40 $^{\circ}$ C. 1. Pentane; 2. Hexane; 3. Heptane; 4. Octane; 5. Nonane; 6. Decane; 7. Undecane; 8. Dodecane; 9. Tridecane; 10. Tetradecane. Analysis is provided in Table 4.

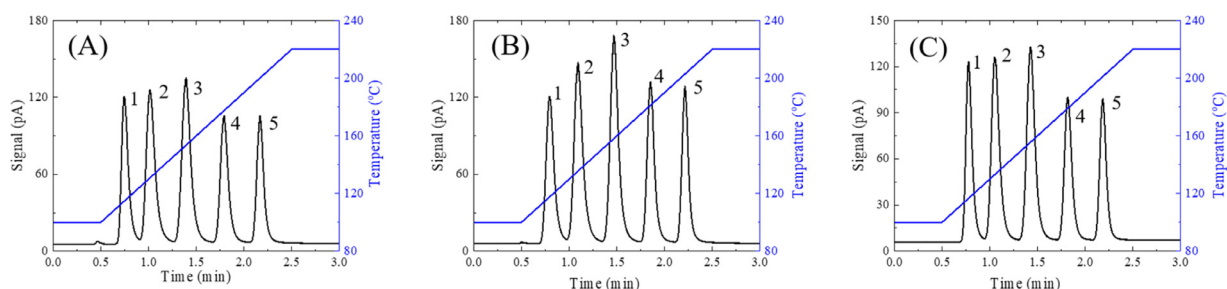


Fig. 6. Example separations of C_{10} – C_{14} alkanes pre-stress testing with no added moisture (A), with 1 μ L of added liquid water (B), and post-stress testing after 100 liquid water injections (C). Splitless injections of 0.025 μ L mixture liquid were made using a carrier gas flow rate of 1.2 mL/min at 100 $^{\circ}$ C. Analysis is provided in Tables 5 and 6.

performance was either not degraded, or only degraded a small amount by liquid moisture injection. Degradation by long-term injection of moisture was also examined via 100 repeated injections of 0.2 μ L of liquid water. The column temperature was set to 120 $^{\circ}$ C during injection with a flow rate of 1.2 mL/min. Injections were made once per minute. Retention times, FWHMs,

and p -values are provided in Table 7, with no significant differences observed after 50 or 100 injections. Analysis of peak capacities (Table 6) corroborates this result, showing that the μ L column does not significantly degrade under long-term moisture exposure.

Table 7

Retention times (RTs), FWHMs, and p -values of C_{10} – C_{14} alkanes prior to stress testing, after 50 injections, and after 100 injections. RTs and FWHMs are provided in minutes. All values are calculated based on 5 runs. p -values were obtained by comparing separations after stress testing with dry separation, with significance taken at $p = 0.05$. p -values are provided as RT/FWHM; no significant differences in RTs or FWHMs were observed.

	RT (Dry)	FWHM (Dry)	RT (50 inj)	FWHM (50 inj)	p -value (50 inj)	RT (100 inj)	FWHM (100 inj)	p -value (100 inj)
C_{10}	0.737	0.0890	0.725	0.0892	0.431/0.824	0.745	0.0846	0.656/0.104
C_{11}	1.000	0.1162	0.983	0.1132	0.420/0.127	1.006	0.1123	0.832/0.082
C_{12}	1.372	0.1196	1.355	0.1172	0.398/0.380	1.378	0.1153	0.840/0.108
C_{13}	1.777	0.1053	1.760	0.1026	0.279/0.380	1.779	0.0999	0.956/0.127
C_{14}	2.158	0.0921	2.140	0.0903	0.180/0.308	2.151	0.0877	0.718/0.080

3. Conclusion

The microfabrication and coating of a chip-based μIL column has been described herein. The μIL column enabled separation of alcohols, chloroalkanes, aromatics, aldehydes, fatty acid methyl esters, and alkanes at temperatures up to 345 °C using dry air as the carrier gas. The column's long-term robustness against oxygen was examined by 48 h of dry air exposure at temperatures up to 220 °C with a degradation of only 8.92% observed. The column also exhibited robustness to moisture, with no observed degradation of separation performance by high moisture concentrations or long-term moisture exposure. The ability to efficiently separate a wide range of both polar and nonpolar compounds along with resilience to moisture and oxygen make the μIL column highly suited for use in portable GC field analysis. While the phosphonium ionic liquid used for the current microcolumn is generally useful for separating various groups of both nonpolar and polar compounds (especially FAMES and alkanes, with efficiencies up to 3132 plates per meter), other ionic liquids could be used for more specialized separations, such as for chiral compounds or essential oils and fragrances. Varying the ionic liquid solution concentration or sodium solution concentration also allows for tuning the coating thickness, therefore tuning separation characteristics as well. Finally, future integration of the μIL column into μGC systems is expected to significantly facilitate development of ultracompact, portable GC devices by alleviating the need for auxiliary carrier gas cartridges and moisture filters.

Declaration of Competing Interest

The authors declare no conflict of interest.

CRediT authorship contribution statement

Maxwell Wei-Hao Li: Conceptualization, Investigation, Methodology, Formal analysis, Data curation, Writing - original draft. **Xiaolu Huang:** Investigation, Formal analysis, Data curation. **Hongbo Zhu:** Conceptualization, Investigation. **Katsuo Kurabayashi:** Data curation, Writing - original draft. **Xudong Fan:** Conceptualization, Investigation, Formal analysis, Data curation, Writing - original draft.

Acknowledgments

The authors acknowledge the support from the Office of the Director of National Intelligence (ODNI), Intelligence Advanced Research Projects Activity (IARPA), via IARPA FA8650-19-C-9101 and from National Institute for Occupational Safety and Health (NIOSH) via R01 OH011082-01A1. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of the ODNI, IARPA, or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright annotation thereon. The authors also acknowledge microfabrication aid from the Lurie Nanofabrication Facility at the University of Michigan.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.chroma.2020.461002](https://doi.org/10.1016/j.chroma.2020.461002).

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