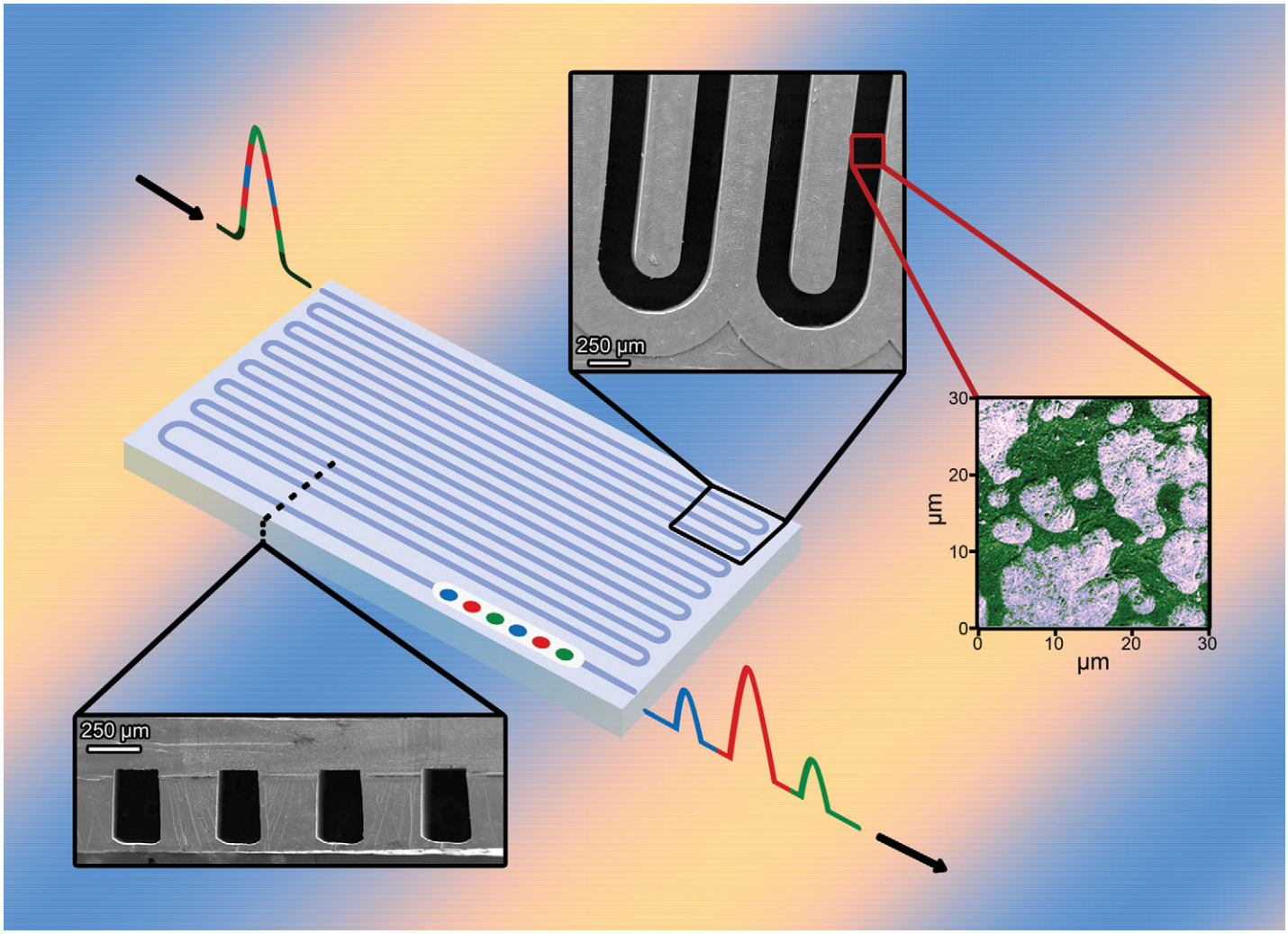

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The development of a disposable gas chromatography microcolumn

The first molded-polymer gas chromatography microcolumn (made of a phase-separated, microtextured thermoset polymer) is described and characterized.

As featured in:

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The development of a disposable gas chromatography microcolumn†

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The first molded gas chromatography (GC) microcolumn is described. This microcolumn consists of a single microtextured thermoset polymer composite which acts as both the structural material and the stationary phase. The resultant microcolumn is inexpensive and has been coupled to a disposable colorimetric sensor array, creating a disposable column-detector unit and demonstrating a proof of concept for a disposable GC microcolumn.

Gas chromatography is the standard technique used for separating and analyzing complex mixtures of volatile or semivolatile compounds. This widespread applicability has encouraged growing interest in the development and commercialization of portable gas chromatographs (GCs) and further miniaturization of GC columns (microcolumns)[1] in both research[2–9] and commercial[10,11] laboratories. Conventional GCs are bulky, have high power consumption, and often have long analysis times. These factors have generally limited GCs to a laboratory environment making *in situ* analysis of field or environmental samples difficult. Ideally, GC miniaturization would yield a small, portable, and low power device that is also inexpensive and easily mass produced; indeed, an ultimate goal might well be the creation of a handheld unit with multiple inexpensive, disposable components (*e.g.*, microcolumn, detector) that could be used multiple times and then discarded.

In the past decade, significant progress has been made in microcolumn separation efficiency, but fabrication processes are essentially unchanged from that used by Angell and Terry in their original micro-GC system.[12,13] In traditional microcolumn design, the column consists of a structural support (*e.g.*, micromachined or photolithographed metal, silicon,[1–7,9,12–14] or parylene[15]) with a separately applied thin film stationary phase (*e.g.*, polydimethylsiloxane (PDMS)). Fabrication of these microcolumns is costly and cumbersome, requiring specialized equipment (*e.g.*, plasma or cleanroom) or hazardous chemicals for lithographic etching.[6,8,12] Even more problematic in column miniaturization is the deposition of the stationary phase,[5,7,12,16–18] which must produce a uniform thin coating that will not delaminate from the structural walls of the microcolumn.

The complexity and cost of fabrication could be substantially reduced if microcolumns were composed of a single polymer or composite that acts as both the structural material and stationary phase. Mold-based fabrication of polymers (*i.e.*, the use of a reusable mold to shape liquid polymer as it sets) is easily scalable and associated with very low fabrication costs.[14,15] In fact, most microfluidic devices and nearly all commercially available polymer products depend on some form of mold-based fabrication. A single standard industrial mold is able to template thousands of polymer pieces; in contrast, current microcolumn fabrication protocols require a patterned, micromachined piece for every microcolumn. There are only a few reports of microcolumns where the support and the stationary phase were the same polymeric material, which unfortunately resulted in extremely limited separation efficiency.[18,19]

This work describes an alternative microcolumn fabrication method in which inexpensive, and even disposable, gas chromatography microcolumns are produced *via* an easily scalable polymer molding process. The potential utility of a colorimetric sensor array as a disposable gas chromatography detector is also demonstrated. This work is the first step to a fully integrated, disposable, and portable gas chromatography column and detector (Fig. 1a). As outlined in Fig. 1b, these microcolumns are fabricated by making a polymer replica of a reusable mold and sealing the microcolumn with a polymer film. The reusable mold was made by micromachining polychlorotrifluoroethylene (PCTFE) with the negative relief of a serpentine channel design (Fig. 2). The resulting PCTFE mold is highly durable, showing no signs of defects after >50 uses. The polymer microcolumns were made by casting a thermoset pre-polymer into the PCTFE mold, degassing under vacuum, and curing. The typical test microcolumns were 1 m long and had rectangular channels that were 250 μm wide and 500 μm tall (Fig. S2a and b, ESI†). After curing, the columns were removed from the mold, sealed with a bottom layer of partially cured

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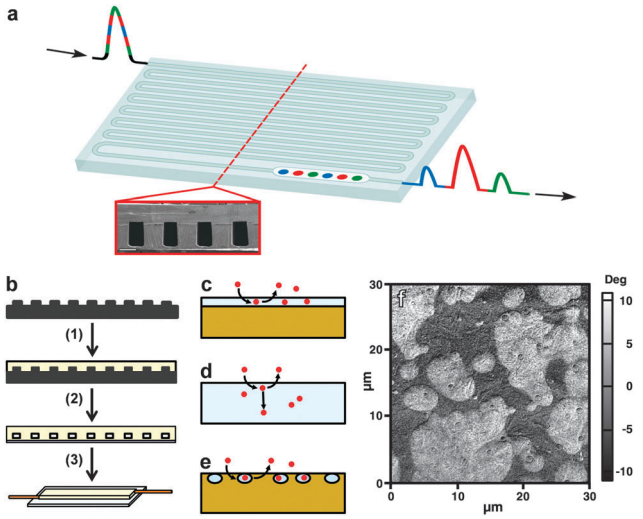

Fig. 1 (a) Concept diagram of a polymer microcolumn integrated with colorimetric sensor array, showing a cross-sectional scanning electron micrograph of the microcolumn's sealed channels (scale bar = 250 μm). (b) Scheme of the polymer microcolumn fabrication process, showing a cross-sectional view of each step: (1) polymerization on the mold forming the serpentine column; (2) sealing of the surface of the serpentine channels; (3) connection *via* silica capillaries to injection port and detector. (c–e) Illustrations depicting analyte interaction with (c) a traditional thin-film column, (d) a highly permeable polymer (*e.g.*, PDMS) column, and (e) a phase separated polymer column. (f) AFM tapping-mode phase image showing the microtexture of a flexible epoxy doped with diethoxydimethylsilane (10 wt%); softer (lighter) domains are seen within a more rigid (darker) matrix.

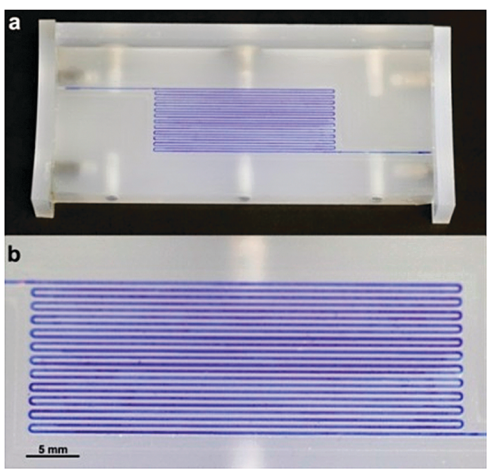

Fig. 2 (a) PCTFE mold, which has removable sidewalls and a serpentine channel design. The raised parts of the mold, which produce the microcolumn channel, are stained for visualization. (b) Expanded view of the mold.

thermoset polymer, and cured further (Fig. S2d, ESI†). Finally, polyimide coated fused silica capillary tubing was inserted into the tapered column inlet and outlet (Fig. S2c, ESI†), secured using epoxy, and connected to a conventional GC–FID (flame ionization detector) system for evaluation.

For conventional GC columns, the choice and thickness of stationary phase polymer is critical for efficient separation. A film that has low analyte affinity or is too thin results in poor separations with analytes co-eluting in the first several seconds after injection. A film that has high analyte affinity or is too thick results in very broad analyte bands and very long retention times. Because a polymer molded microcolumn has no coated thin film stationary phase, material permeability must be considered. A microcolumn made from a polymer that is too permeable (*e.g.*, PDMS), will yield very broad analyte bands, poor resolution, and extremely long retention times (Fig. S3a, ESI†). Alternatively, a microcolumn made from a polymer that is too impermeable (*e.g.*, epoxy) has poor resolution, low peak capacity, and very short retention times (Fig. S3b, ESI†). An ideal polymer microcolumn would be made from a polymer composite that self-segregates into permeable and impermeable surface domains upon curing. The phase-separation of polymer mixtures during curing, and the surface segregation of one component in a two-component polymer formulation have been observed previously in various polymer composites.[20–22] Polymer processing characteristics must also be considered. To avoid formation of gas bubbles in the curing polymer (which create flow path imperfections, band broadening, and multiple peaks per component, *cf.* Fig. S3c, ESI†), a proper polymer precursor must have a low viscosity and a cure time sufficient to permit degassing (*e.g.*, >30 min).

The proposed separation process of analytes for highly permeable single-polymer microcolumns, impermeable single-polymer microcolumns, and phase-separated dual-polymer microcolumns is illustrated in Fig. 1c–e. For a conventional thin-film column (Fig. 1c), the impermeable structural support limits analyte diffusion to a depth equal to the film thickness. In contrast, as shown in Fig. 1d, a highly permeable polymer (*e.g.*, PDMS) microcolumn has no impermeable barrier to stop analyte diffusion, and analytes penetrate far into the polymer matrix, producing a chromatogram with broad peaks and long retention times. The intent here is the creation of a new class of chromatographic separation using a phase-separated polymer column (Fig. 1e), where the permeable domains are generally confined within a non-permeable matrix and analyte permeation is restricted to the top few microns, mimicking a traditional thin film column.

By doping an organosilane into a nonpermeable flexible epoxy, a microcolumn that capitalizes on the phase-separation and surface segregation phenomenon (previously discussed) has been successfully created. A flexible epoxy doped with 10 wt% diethoxydimethylsilane (which is easily molded) shows phase-separation upon curing, as shown in the AFM phase image (Fig. 1f, discussion in ESI†) and shows surface segregation of the siloxane-rich phase, as shown in the TOF-SIMS spectra (Fig. S4, discussion in ESI†).[23] It is proposed that these siloxane-rich domains act as the stationary phase of the microcolumn while the siloxane-poor epoxy network serves as the structural support. Molding of this formulation generates microfluidic channels that are uniform, with high conformity and without defects (Fig. S2 and S5, ESI†). This work serves as an initial exploration of phase-separated all-polymer gas chromatography microcolumns. Further discussion of the polymer formulation used here can be found in the ESI†.

To probe the separation performance of a doped epoxy microcolumn (250 × 500 μm × 1 m), a mixture of *n*-alkanes,

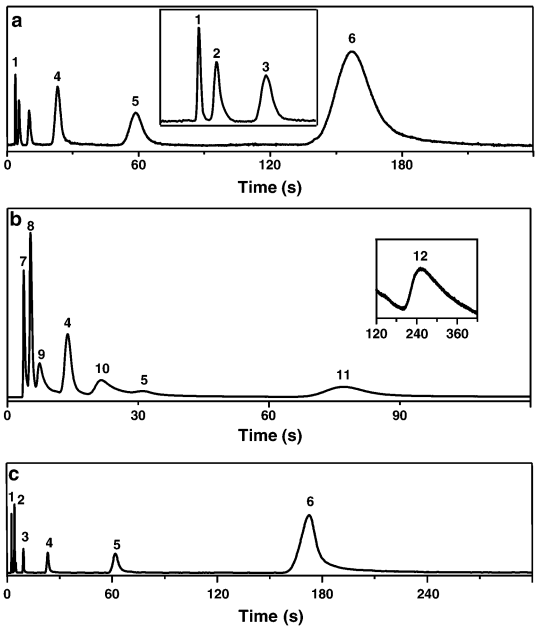

Fig. 3 Chromatograms obtained using a diethoxydimethylsilane doped epoxy microcolumn. (a) Separation of *n*-alkanes using a 1 m long microcolumn with a cross-section of 250 μm width × 500 μm height at room temperature (u = 30 cm s^{-1} = linear velocity; F = 2.3 mL min^{-1} = flow rate); the inset shows an expanded scale of the separation and resolution of the earliest analytes during 0 to 15 s. (b) Separation of eight VOCs using microcolumn in (a) at 35 °C (u = 40 cm s^{-1}; F = 3 mL min^{-1}). (c) Separation of *n*-alkanes using a 1 m long microcolumn with a cross-section of 100 μm width × 500 μm height at room temperature (u = 55 cm s^{-1}, F = 1.7 mL min^{-1}). A theoretical plate count of 1800 is observed. (1) *n*-Pentane, (2) *n*-hexane, (3) *n*-heptane, (4) *n*-octane, (5) *n*-nonane, (6) *n*-decane, (7) acetone, (8) 1,1,1-trichloroethane, (9) trichloroethylene, (10) ethylbenzene, (11) 1,2-dichlorobenzene, and (12) 1-nonanal (inset).

C_5–C_{10}, was injected onto the column. At room temperature, the components are easily separated in less than 180 seconds, showing six well-resolved peaks with baseline or near baseline resolution for all analytes (Fig. 3a, Table S1, ESI†). The peak capacity (the number of equally well-resolved peaks that can be distinguished between two defined retention times) is 22 between C_1 and C_{10}. All peak shapes are more than adequate with tailing factors (T_f) well below two (T_f = 1.45 for the worst tailing alkane, decane), and the effective number of theoretical plates is >400 m^{-1} as measured by the decane peak using the full width at half maximum. Separation of a mixture of eight VOCs (including ketones, aromatics, aldehydes, and halogenated alkanes) has also been achieved isothermally at 35 °C (Fig. 3b); high boiling point analytes such as 1-nonanal (b.p. 195 °C) can be eluted relatively quickly (<5 min) even without temperature programming. The plates per meter is improved to 1800 m^{-1} simply by reducing the channel dimensions to 100 × 500 μm (Fig. 3c, Table S1, ESI†).

For comparison, optimized traditional microcolumns previously reported in the literature range from ~500 to 5000 plates per m.[7,8,18–20] Though not the top preforming microcolumn, these microcolumns are able to separate simple mixtures at a substantially decreased cost, and may find utility where an initial rapid, inexpensive, and cursory analysis of field samples is necessary (*e.g.*, military, overseas, or educational applications). It is expected that further optimization of the channel dimensions, polymer composition, and polymer microstructure will lead to substantial improvements in column efficiency (*cf.* ESI†). Similarly, fabrication of compact multi-meter length microcolumns is entirely feasible by the polymer molding process. Although these microcolumns are inexpensive enough to be used once and discarded, multiple uses over a period of 50 days does not significantly change a microcolumn's performance (Fig. S6, ESI†).

Previously reported microdetectors are generally expensive or power demanding, and most do not provide chemical identification.[9,12,24–27] Chemiresistor sensor arrays have previously been utilized as microdetectors for gas chromatography; they do provide some chemical information and have shown some promising results for deconvoluting co-elutions.[28,29] We have previously reported disposable, highly sensitive colorimetric sensor arrays for the detection and identification of VOCs and toxic gases.[30–34] This technique, though exceptional at fingerprinting complex mixtures,[34–36] cannot produce a component-by-component mixture analysis. Coupling a microtextured polymeric microcolumn and a colorimetric sensor array may prove useful as an inexpensive, even disposable, technology for the component-by-component analysis and chemical identification of mixtures.

To probe the feasibility of a colorimetric sensor for GC, a mixture of three amines was injected onto the previously described microcolumn at room temperature, and the response of the eluent was recorded with either an FID or a colorimetric sensor array. The array response is dependent on analyte concentration, and therefore, one expects the largest change in ED to occur when the highest concentration of analyte passes over the detector, *i.e.*, at each analyte's retention time. Plotting the ED of the slope of sensor response *versus* time for the colorimetric array signal yields a chromatogram strikingly similar to that obtained using an FID detector (Fig. 4 and Fig. S7, ESI†). See ESI† for details of the experimental, image processing, data analysis, and array response. These results demonstrate a respectable proof of concept for a disposable GC microcolumn-colorimetric detector unit.

In this work, we have demonstrated a new approach to microcolumn fabrication. The use of microtextured polymer composites has allowed us to easily fabricate gas chromatography microcolumns through molding from a micromachined master. These microcolumns have no separately applied thin film stationary phase: the polymer composite phase self-segregates into structural and functional domains. This inexpensive and disposable GC microcolumn is capable of separating mixtures of VOCs with baseline resolution in seconds to minutes. We have also coupled this disposable micro-GC column with a disposable colorimetric sensor array. While further work is necessary to fully realize this technology's potential, this work demonstrates a respectable proof of concept for a disposable GC microcolumn.

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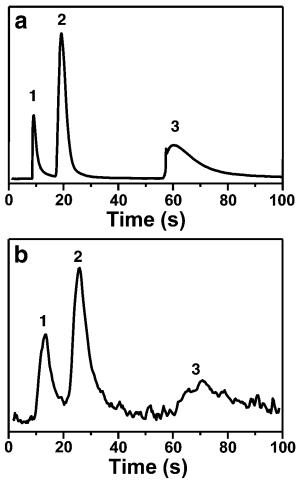

Fig. 4 Comparison of detectors for the separation of amines at room temperature using a doped epoxy microcolumn. (a) Flame ionization detector: FID signal *vs.* time, u = 30 cm s^{-1}; F = 2.3 mL min^{-1}. (b) Colorimetric sensor array: Euclidean distance of the slope response *vs.* time, u = 30 cm s^{-1}; F = 2.3 mL min^{-1}. (1) Propylamine, (2) triethylamine, and (3) piperidine.

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