FIELD TESTING OF A RUGGED MEMS GAS CHROMATOGRAPH PROTOTYPE: SELECTIVE ANALYSIS OF TRACE-LEVEL TCE VAPORS IN CONTAMINATED HOMES

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ABSTRACT
Two fully integrated and automatically controlled MEMS gas chromatographs (µGC) were successfully deployed in the field to monitor trichloroethylene (TCE) at trace-level concentrations (0.6-80 ppb) in homes suffering from vapor intrusion (VI) from surrounding TCE-contaminated soil. Each instrument combines a high-volume sampling module (non-microfabricated) with a microanalytical module consisting of a microfocuser, dual microcolumns, and a chemiresistor array detector. A complete sampling and analytical cycle requires 15-30 min, depending on required sensitivity. Limits of detection as low as 0.02 ppb were achieved. TCE was separated from 45 co-contaminants. Use of the prototypes in fixed-site (temporal TCE fluctuations) and portable operating modes (spatial mapping of TCE) was successfully demonstrated. Good agreement with concentrations determined with standard reference methods was achieved.

KEYWORDS
Micro Gas Chromatograph, µGC, Sensor Array, Microsystem, Vapor Analysis, Trichloroethylene

INTRODUCTION
Human exposure to volatile organic compounds (VOCs) in the general environment, where concentrations are typically low (i.e., < 100 ppb) [1-3], can lead to adverse acute or chronic health effects, including respiratory tract irritation, central nervous system depression, worsening of asthma [4-5], cancer, or damage to the liver or kidneys [6].

Vapor intrusion (VI) has been identified as a potential mechanism for exposure of the general population to VOCs. VI is a term used to describe the entry of VOCs into residential or office buildings from surrounding contaminated soils or groundwater. The pathways for VI contamination of indoor air typically involve permeation or penetration through sub-surface walls, and are considered separate from indoor air contamination arising from sources within the building or from infiltration of ambient air contaminants. VI is an emerging problem in the U.S., the extent of which has only recently been recognized by Department of Defense (DoD), regulators, private industry and others.

Trichloroethylene (TCE) is the most common contaminant of concern at VI-impacted DoD sites. It was used as a solvent for cleaning of metal parts and was released into the environment, during 1960’s and 1970’s [7-9]. TCE can seep down through soil to underlying groundwater sources, and then migrate a substantial distance from the original discharge point [10]. Due to its relatively high vapor pressure (69 torr at 25 °C), it can volatilize, permeate up through porous soil, and into overlying structures. Recognition of this problem has led the U.S. Air Force to set a mitigation action level (MAL) of 2.3 ppb for residential buildings on, or near, bases.

U.S. EPA Method TO-15 uses Summa canisters for sample collection followed by GC-FID or GC-MS analysis, and it is the standard method to quantify low-level indoor VOCs suspected of arising from VI. However, the usual shortcomings associated with time-integrated sampling and subsequent laboratory analyses limit the quantity and quality of data available to guide VI investigations and interventions. The current standard 24-hour collection period used for TO-15 does not capture temporal variations in exposure to the residents. Also, the delay between sampling and laboratory analysis precludes timely response or remediation efforts. Furthermore, background VOCs in indoor air, associated with household products or human activities, can make it difficult to differentiate such sources of TCE from that generated by VI. This, in turn, has an impact on the nature of mitigation efforts implemented. Thus, there are several drivers for developing portable or permanently installed on-site analytical systems that can accurately determine TCE (or other VOCs of interest) at the low- or sub-ppb concentrations prevalent in most VI-impacted residences in the presence of other background VOCs.

Gas chromatographic microsystems (µGC) have the potential to meet this need. The past decade has seen many reports on the components of µGC systems, including micropreconcentrators, microcolumns, and microsensor array detectors [11-13]. Fewer reports have appeared, however, on fully integrated µGC systems [14-17].

Here, we describe a field deployable µGC prototype (referred to as “SPIRON”) tailored for the determination of TCE in near-real-time in the presence of common background VOCs. Field calibrations, comparison of results with those of reference methods in TCE-contaminated homes, and the use of SPIRON to monitor temporal and spatial fluctuations in TCE concentrations with an analytical cycle time of 15-30 min are presented.
EXPERIMENT

SPIRON μGC

Figure 1 shows the SPIRON μGC and its major components. It has two main subsystems. One is the analytical subsystem including a single-stage microfocusor (μF), two 3-m long microcolumns, and a microfabricated chemiresistor (CR) sensor array, and the other is the front-end sampling subsystem, which includes a pretrap and sampler (non-MEMS), two commercial mini-pumps (KNF, Trenton, NJ), and a manifold with six commercial mini-valves (Lee Co., Westbrook, CT).

![Image of SPIRON μGC and its major components.](Image)

The single-stage μF has a $3.2 \times 3.45 \times 0.5$ mm DRIE-Si cavity that holds ~2.3 mg of the graphitized carbon adsorbent, Carbopack X (Supelco, Bellefonte, PA) and overall dimensions of $9.76 \times 4.18 \times 0.6$ mm. The device was capped with Pyrex plate using anodic bonding. For bulk resistive heating, Cr/Au contact pads were evaporated onto its backside and a Ti/Pt resistive temperature device (RTD) was patterned near the contacts for monitoring temperature.

Fabrication and stationary-phase deposition methods for microcolumns used in this study have been described in a previous study [18]. Rectangular channels (150 μm (W) × 240 μm (D)) were formed in Si wafers by DRIE in a previous study [18]. Rectangular channels (150 μm (W) × 240 μm (D)) were formed in Si wafers by DRIE in a previous study [18]. Rectangular channels (150 μm (W) × 240 μm (D)) were formed in Si wafers by DRIE in a previous study [18]. Rectangular channels (150 μm (W) × 240 μm (D)) were formed in Si wafers by DRIE in a previous study [18].

The chemiresistor (CR) array has eight Au/Cr interdigital electrodes (IDEs) with $4 \times 2$ layout on thermally grown SiO$_2$. Each IDE has 24 finger pairs with 5 μm width and spacing and 0.5 mm finger lengths. Thiolute-monolayer-protected gold nanoparticle (MPNs) films as sensing materials on interdigital electrodes give differential responses for the different sensors; thiols used in this study were n-octanethiol (C8), 1-mercapto-6-phenoxylhexane (OPH), methyl 6-mercaptotriheptanoate (HME), and 4-mercaptopiphenyl-acetylene (DPA). Two sensors were coated with each MPN for redundancy. To form a detection cell (internal volume of ~3 μL), the CR array was lidded with a piece of Macor having flow channels and capillary connections as inlet and outlet.

In the front-end sampling subsystem, an upstream high-volume sampler (non-MEMS, resistively-heated metal tube packed with 100 mg of Carbopack X) is employed to achieve ppt-level detection limits with a sampling volume of < 20 L, and a pre-trap (50 mg of Carbopack B) is used upstream from the sampler to exclude low-volatility interferences. These devices were optimized for selective TCE sampling in a previous study [19]. Two mini-pumps and a manifold with six mini-valves were appropriately actuated for sampling, focusing, and separation flows. Scrubbed air is used as the carrier gas. All functions are controlled by LabView routines written in-house.

An analytical cycle consists of four steps. First, an air sample is drawn through manifold-mounted pretrap and sampler at a high flow rate (~1 L/min), bypassing the other components. Second, the VOCs captured on the sampler are thermally desorbed and focused onto the μF at a low flow rate (~20 mL/min). Then, the μF is rapidly heated to inject the VOCs onto the first microcolumn for separation and detection of eluting peaks by the sensors in the CR array. Finally, components of VOC mixtures are identified and differentiated by virtue of the response patterns from the CR array and retention time for each vapor.

Characterization of the μGC

The SPIRON μGC system was first characterized in the laboratory prior to being deployed in the field. This included calibration using standard samples (range: 10-430 ng), determination of limits of detection (LODs), and establishing reproducibility of retention times and responses. Challenges with low concentrations of TCE were also performed, in addition to separating TCE from a large number of indoor VOC air contaminants, using test atmospheres generated at room temperature. In the field, the μGC was also calibrated with standard samples (range: 25-310 ng) from a compressed gas cylinder containing 11 ppb of TCE in air, and LODs were determined.

Field study

The field application of the μGC was performed in a house just south of Hill Air Force Base (AFB), overlying a shallow TCE groundwater plume originating at the base. Prof. Paul Johnson of Arizona State University (ASU)
operates this VI study house for a Strategic Environmental Research and Development (SERDP) project. Two µGCs were deployed in the house. Samples were collected throughout the house, but the majority were in the basement near a significant VI entry area. The extent of TCE VI was intentionally increased periodically by reducing the pressure (relative to sub-slab) inside of the house using a variable speed fan mounted in a 1st-floor window. Differential pressure between the house and the sub-slab was monitored using a differential pressure recorder (Omniguard 4, Engin. Solutions, Inc., Lynnwood, WA). For tests of portable operation, sampling and analysis were also performed in a second house in the vicinity of Hill AFB in which there was an intentionally placed TCE indoor source, instead of TCE from VI. For some SPIRON samples, concurrent EPA TO-15 canister samples (6 L) were collected within 30 cm of the SPIRON µGC for reference. Samples were also collected periodically with a Hapsite portable GC-MS also located near the SPIRON prototype.

RESULT AND DISCUSSION

Laboratory characterization of the µGC

The µGC system was first characterized in the laboratory. TCE calibrations were linear (range: 10-430 ng; R² > 0.99 for all sensors), LODs ranged from 0.04 ppb (OPH) to 0.12 ppb (DPA) in a 20-L sample, short-term sensor-array response (i.e., peak area) variability was < 9% (n=10), and retention time variability was < 1% (n=10). As shown in Figure 2, separation of TCE from 45 other VOCs was possible in < 60 sec and unique response patterns were obtained. TCE was measured at 100 ppt from a 20-L air sample with responses from three of the four sensors. One µGC prototype was used in portable operation in order to spatially map TCE concentrations (0.6-80 ppb) throughout a second house near Hill AFB and to find where a TCE source had been intentionally placed (hidden). Figure 5 shows the distribution of TCE concentrations in the house. The measurement sequence started on the 1st floor first, where concentrations were low, and continued in the basement. Finally, the µGC succeeded in locating the TCE source, which had been placed in the closet of a room in the basement.

Field application of the µGC

In the field, re-calibration was performed using a compressed-gas TCE standard over a range of captured sample masses from 5-60 ppb-L (26-312 ng) and again gave linear response curves with results falling within 10 % on average of the reference method, EPA TO-15 (Fig. 3). At lower concentrations there was a positive bias. LODs at the field test location ranged from 0.022 ppb (HME) to 0.20 ppb (DPA) in 20-L sample.

Both µGCs were tested in the study house in fixed site operation. The representative set of results in Fig. 4 show that TCE concentrations measured by the SPIRON µGCs track the changes in pressure, and agree closely with results from two reference methods (EPA TO-15 and Hapsite portable GC-MS).

CONCLUSIONS

A fully integrated and automated µGC tailored for the determination of trace-level TCE in houses affected by TCE VI has been successfully developed, characterized and tested in the field. Responses to TCE are linear with concentration, and provide an LOD as low as 0.022 ppb. The detection of 0.1 ppb of TCE was demonstrated with a 20-L sample in a total analysis time of 30 min. Selective measurement of TCE in the presence of 45 co-contaminants was demonstrated. Temporal and spatial variations in low-ppb TCE air concentrations were...
accurately tracked; agreement with reference-method determinations was within 10%, on average.

Figure 5. TCE concentrations in a house in which a point source of TCE was located – determined with the SPIRON µGC in portable operation.

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