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Meso-Scale VOC-Mixture Analyzer with Tunable Separation and Microsensor Array Detection

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Abstract: A novel portable instrument developed for field determinations of complex mixtures of volatile organic compounds (VOCs) is described. The key features of the instrument are a miniature multi-stage adsorbent preconcentrator/focuser, two series-coupled separation columns with pressure and temperature tunable retention control, and an integrated array of four chemiresistor (CR) sensors coated with Au-thiolate monolayer-protected nanoparticles (MPN). MPN-CR array response patterns are used with retention times to identify eluting vapors. Air is used as the carrier gas. Calibrations of 20 common indoor air contaminants gave LODs in the range of 0.05 ng/g~0.53 ng/g for a 1 L sample volume. Results of preliminary analyses of characteristic VOCs generated from U.S. currency as well as vapor-phase markers of environmental tobacco smoke (ETS) at low- or sub- ng/g levels are presented.

Key words: microsensor; gas chromatography; nanoparticle; sensor array; portable; ETS

1 Introduction

Most field determinations of volatile organic compounds (VOC) rely on adsorbent-tube sampling followed by gas-chromatography/mass-spectrometry (GC/MS) analysis[1]. While reliable, the costs and delays between sampling and analysis inherently limit the quality, quantity, and frequency of data collected in field investigations. Numerous portable instruments are available for field VOC detection, but few are amenable to rapid, quantitative analyses of multiple trace-level contaminants due to their size, cost, and/or limited sensitivity[2~4].

This paper describes the design, operation, and laboratory testing of a novel prototype portable GC suitable for routine, near-real-time determinations of the components of complex VOC mixtures at low- or sub-parts-per-billion (ng/g) concentrations. The key components of the instrument are a miniature multi-adsorbent preconcentrator/focuser (PCF); a dual-column, high-speed separation module with tunable retention capabilities; and a detector comprising an array of chemiresistor (CR) sensors coated with gold-thiolate monolayer-protected nanoparticle (MPN) that provides a characteristic 'fingerprint' of each analyte. Scrubbed ambient air is used as the carrier gas.

Previous testing of a 1st-generation prototype instrument established some of the advantages accruing from combining tunable separations with sensor-array detection[5]. For this study, the polymer-coated surface-acoustic wave (SAW) sensor array used in the 1st-generation prototype was replaced with a CR sensor array and calibrations of 20 common indoor air contaminants were performed. Tests were then performed with a 2nd-generation instrument, which incorporates several enhancements in design and operating features. Preliminary laboratory tests are presented that explore the feasibility of using this instrument to solve two interesting problems: analyzing 'signature' VOCs emitted by U. S. paper currency and analyzing selected markers of environmental tobacco smoke (ETS) at trace levels.

U.S. Customs requires declaration of currency valued at >$10 000 leaving or entering the country[6]. Illegal transport of currency across the U. S. border is currently monitored with dogs trained to smell vapor-phase components of currency inks. Limitations of canine detection methods include olfactory fatigue and the time and effort required by personnel to supervise and care for the dogs. Straight-chain aldehydes are produced from the curing process of currency ink and have been shown to serve as good 'signature' VOCs[7]. Field instrumentation capable of rapid detection of such characteristic VOCs would facilitate screening cargo at border crossings.

ETS is a complex mixture of > 4 000 chemicals[8]. It is classified as a human carcinogen. The complexity of ETS and the presence of confounding sources has prompted the use of marker compounds such as 3-ethenylpyridine (3-EP) to estimate ETS levels[8]. Concentrations of 3-EP in indoor environments where smoking is allowed can be as high as 1.5 ng/g[9~11]. Another vapor, 2,5-dimethylfuran (2,5-DMF), has been used as an ETS marker in air and in breath[12].

2 Experimental

2.1 Instrument features

Based on studies with the 1st-generation prototype, a 2nd-generation prototype (Fig.1) was fabricated with enhancements in critical components, fluidic layout, and software. Both prototypes have similar preconcentration and separation modules, and both were constructed by collaborators at Microsensor Systems, Inc. (Bowling Green, KY). The PCF consists of a 1.32 mm i.d. stainless steel tube typically packed with 8 mg of Carbopack B, 2.5 mg of Carbopack X, and 1.8 mg of Carboxen 1000 (Supelco, Bellefonte, PA). A coil of insulated Cu wire is used for heating (>150℃/s). The first column is a fused-silica capillary (0.25 mm i.d. × 4.5 m) with a PDMS bonded stationary phase (0.5 μm). The second column (same dimensions) has a moderately polar polytrifluoropropylmethylsiloxane bonded phase (0.25 μm). Each column is coiled together with a heating wire and thermocouple in an "at-column heating" configuration (RVM Scientific, Santa Barbara, CA) allowing independent column heating at rates of up to 1000℃/min. A valve connected to the junction point of the two columns can be closed periodically to let the carrier gas bypass the first column, causing faster elution for vapors already in the second column and slower elution for those still in the first column. This "pressure tuning" can enhance separations [13].

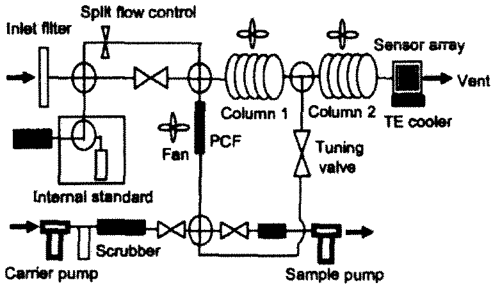

Fig.1 Schematic of 2nd-generation instrument

The CR array that replaces the SAW sensor array as the detector consists of four interdigital metal electrodes on an insulting substrate, capped with a Macor® lid (cell volume ~ 3 μl) fitted with inlet/ outlet capillaries. Vapors partitioning into an MPN film on a CR sensor cause it to swell, which changes the electron tunneling barrier and thereby the film resistance[14~19].

Data acquisition and processing for the 1st- generation prototype are described in reference [5]. A Labview™ program run from a laptop computer controls the 2nd-generation instrument, and acquired data files are treated in Grams 32 (Galactic Industries, Salem, NH).

2.2 Calibration

The 1st-generation instrument was calibrated with 20 common indoor air contaminants in three subsets of 6-7 vapors that could be easily resolved chromatographically. For these tests only three CR sensors were used, spray-coated with films of MPNs derived from n-octanethiol (C8), 1-mercapto-6-phenoxy-hexane (OPH), and 7-mercaptoheptanitrile (CCN), respectively. A test atmosphere of the vapor mixture was generated in a Tedlar® bag, diluted with sufficient clean air to produce μg/g-range concentrations. Gas-tight syringe aliquots were drawn from the bag and injected into a flow of scrubbed air as it was drawn into the instrument. Effective (mass-equivalent) vapor concentrations were calculated according to the ratio of injection and sample volumes and ranged from 0.4~30(ng·g^{-1})/L. Three replicates were run at each concentration .

2.3 Analysis of currency vapors and ETS markers

For tests of 'signature' vapors from U. S. currency performed in this study, 300 new $1 bills were sealed in a Tedlar bag to which 5 L of N_2 gas was added. Using the 2nd-generation instrument, preconcentrated samples (0.5 L volume) were collected at 0.13 L/min, thermally desorbed at 300℃ onto the first separation column at an injection split ratio of 7:1 and eluted at 1 ml/min. Parallel adsorbent-tube samples were collected and analyzed by EPA Method TO-17[1].

For tests of ETS markers, it was necessary to substitute the isomer 4-EP for 3-EP because the latter is not available commercially. Retention and response factors for these isomers are reported to be equivalent[20]. Test atmospheres of 2,5-DMF and 4-EP, along with 14 common co-contaminants found in smoking environments, were generated in Tedlar bags and injected into the prototype as described above.

3 Results and Discussion

3.1 Calibration of 1st-generation prototype

With the exceptions of tridecane and tetradecane, which showed evidence of incomplete desorption from the PCF, calibration curves (peak area vs. conc.) were linear over the concentration ranges tested (r^2>0.99). Limits of detection (LOD) ranged from 0.05 ng/g to 0.53 ng/g from the most sensitive sensor. LODs for this CR array ranged from 4~33 times lower than those from the SAW sensor array obtained under similar GC conditions. LODs varied directly with vapor pressure except for the very low volatility compounds (e.g., tridecane), which showed significant peak broadening. Table 1 presents retention times, LODs, and normalized response ratios (patterns) for a representative subset of vapors. Ratios were normalized by dividing sensitivities (slopes of peak area vs conc.) for a given vapor by that for the most sensitive sensor in the array. Response patterns of vapors from different classes were distinct (e.g., aromatics vs. alkanes). Combining response patterns with retention times leads to accurate vapor recognition.

Table 1 Subset of LODs and normalized response patterns

Vapor	p_v ×133 Pa	RT^a /s	LOD^b /ng·g^{-1}	Response pattern C8	OPH	CCN
Toluene	28	123	0.53	0.61	1.0	0.97
PCE	19	136	0.32	0.91	1.0	0.83
N-nonane	5	228	0.29	1.0	0.79	0.30
Mesitylene	3	245	0.09	0.84	1.0	0.97
D-limonene	2	339	0.05	0.40	0.37	1.0
N-undecane	0.4	359	0.09	1.0	0.60	0.28
N-tridecane	0.06	482	0.16	1.0	0.46	0.20

^{a} retention time; ^{b}1L sample volume

3.2 Signature vapors of U. S. currency

The headspace over the sample of $1 bills was analyzed using the 2nd-generation instrument. In this case, the fourth CR sensor was coated with an MPN having a monolayer of 4-diphenylacetylene thiolate (DPA). Chromatograms contained 10 significant peaks (Fig.2) identified from parallel GC/MS analysis and correlated with their retention times and CR-array response patterns. Five 'signature' straight-chain aldehydes (C_5-C_9) were present at relatively high concentrations (20 ng/g~300 ng/g). Calibrations were performed on authentic samples of these compounds and LODs were determined to be in the low- or sub-ng/g range.

3.3 Determination of ETS markers

An adsorbent pre-trap containing a low-surface-area adsorbent was developed and used to retain high-boiling vapors that are not efficiently desorbed from the PCF, while allowing target vapors and interfering vapors of similar volatility to pass through to the PCF for analysis. Separation conditions were developed to resolve 2,5-DMF and 4-EP from the 14 most prominent co-contaminants of similar retention range determined from field and chamber samples of ETS analyzed by GC/MS. A CR array coated with C8, OPH, CCN, and an MPN derived from methyl 6-mercaptohexanoate (HME) was used. Fig.3 shows the four CR GC traces for all 16 vapors as well as the response patterns of the two markers. The 4-EP response pattern is unique. LODs for 2,5-DMF and 4-EP are 0.58 (ng·g^{-1})/L and 0.08 (ng·g^{-1})/L, respectively.

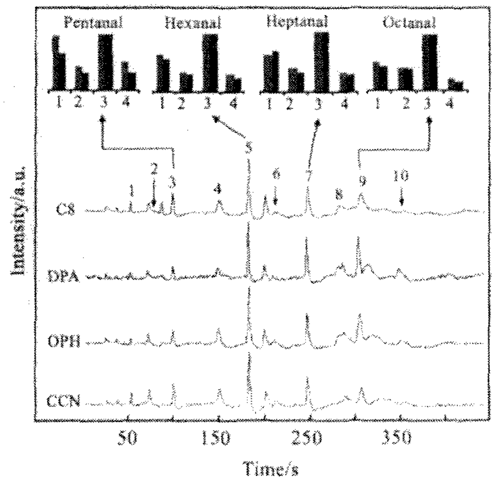

Fig.2 4-CR GC traces an response patterns of signature COCs of a 0.5 L headspace sample collected above 300 US $ 1 bills; sensor number: 1-C8; 2-DPA; 3-OPH; 4-CCN; response bar chart: headspace sample (blue), calibration (red)

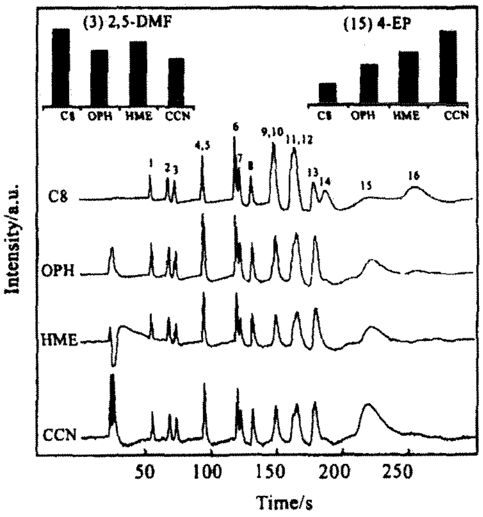

Fig.3 4-CR GC traces of ETS markers and 14 co-contaminants and response patterns of 2,5-DMF and 4-EP

4 Summary

This is the first published demonstration of a portable instrument capable of determining markers of ETS and characteristic vapors generated from U.S. currency at trace levels among common interfering vapors. LODs for these and other VOCs commonly found as indoor air contaminants are in the low-ng/g or high-parts-per-trillion(ppt) range. The combination of (selective) preconcentration, chromatographic separation, and microsensor array response patterns leads to effective multi-vapor analysis with typical cycle times of $\leq$15 minutes.

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