# MEMS Gas Chromatograph for Explosive Marker Compounds: Temperature and Flow Rate Effects on Sensor-Array Detector Responses and System Performance

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A gas chromatographic microanalytical system (μGC) optimized for near-real-time determinations of sub-ppb vapor concentrations of selected marker compounds of explosives is demonstrated. This μGC, uses micromachined components to selectively focus, inject, separate and detect/recognize the markers, and uses conventional components for high-volume sampling, valving, and pumping. Building on our laboratory prototype reported previously [1], here we present results from a study examining the tradeoffs in overall performance as a function of flow rate and operating temperature, with a focus on the microsensor array used as the detector. The target compounds are 2,4- and 2,6-dinitrotoluene (2,4- and 2,6-DNT; TNT markers) and 2,3-dimethyl-2,3-dinitrobutane (DMNB; a taggant). Limits of detection (LOD) $\leq$ 3 ng, separation from similarly volatile alkane (fuel) interferences, and a total separation time of < 1 min have been achieved. Complementing earlier μGC systems reported by our group [2-3] and by others [4-5], this μGC has been optimized for rapid determinations of trace-level explosive markers, suitable for airport screening applications.

The 8-element chemiresistor (CR) array detector uses thiolate-monolayer-protected gold nanoparticle (MPN) films as the interface layers, whose response patterns assist in differentiating markers from interferences [5]. The MPNs have ligands derived from the following: n-octanethiol (C8), 6-phenoxyhexane-1-thiol (OPH), 4-(phenylethynyl)-benzenethiol (DPA), methyl-6-mercaptohexanoate (HME), each coated on a pair of array sensors. To prevent excessive peak broadening, due to slow diffusion rates of the targets into the MPN films and other factors, operating the CR array at elevated temperature was required.

Results show that increasing the array temperature from 55-80°C (1.2 mL/min) led to sensitivity decreases of up to 6-fold and LOD increases of up to 5-fold due to a reduction in the mass uptake in the MPN films. Diffusion rates increased and peaks sharpened over this temperature range, causing resolution increases up to 4-fold. Increasing the flow rate from 1.1-3.7 mL/min (70°C) led to a decrease in peak area of up to 3-fold due to dilution by the carrier gas and lags in the sorption/desorption rates in the films. Interestingly, decreases in peak widths and increases in peak heights were observed, which led to LOD *decreases* for 2,4-DNT and 2,6-DNT of up to 2-fold. For DMNB, peak height passed through a maximum over this flow rate range, leading to a net 2-fold increase in the LOD. A slight increase in resolution between 2,4-DNT and 2,6-DNT was observed. Deciding on the final operating conditions of the μGC required consideration of the tradeoffs not only for the sensor array, but also for the microfocuser (μF) and microcolumn. Taking LODs, analysis time, μF capacity and injection bandwidth, as well as chromatographic resolution into account, a baseline system temperature of 70°C and analytical flow rate of 3 mL/min were selected. At these settings, sensor responses were stable for 11 days (8 hrs/day) in air, with < 2% sensitivity drift per day. A simple mixture of the two primary markers and a set of $C_{10}$-$C_{14}$ alkanes (model jet fuel compounds) was nearly-baseline resolved with the full microanalytical system, (μF, microcolumn, and CR array) using a temperature programmed separation (see Figure 1). Calibrations of this system yielded LODs of ~1-3 ng which correspond to 0.06-0.3 ppb for the markers in a 1-L preconcentrated air sample. LODs of 12-19 ng were obtained for the interferences, illustrating the partial selectivity of the array for the markers. These operating conditions are being used in field prototype μGC.

**References:**

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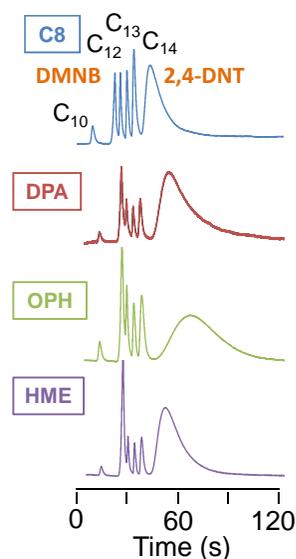
*Figure 1. μGC separation of the explosive markers, DMNB and 2,4-DNT, and interfering model fuel cmpds.*