

Supplemental Document

Gas Chromatography/Mass Spectrometry (GC/MS) Analysis.

Approximately 2 grams of each consumer product was added to individual, clean 0.5 liter custom-modified glass sidearm bottles that initially contained only ambient laboratory air. The bottles were sealed with Teflon-lined screw caps, and volatile constituents in the products were allowed to equilibrate into the headspace of the flask for at least 24 hours at room temperature. Each bottle's sidearm was fitted with a septum that allowed for the withdrawal of headspace vapors using a gas-tight syringe. Consumer product samples were sealed inside the bottles and stored at room temperature for no more than 21 days before analysis.

Samples (1 – 10 mL aliquots at approximately $T = 22^{\circ}\text{C}$ and $P = 750 \text{ mm Hg}$) were analyzed for VOCs using an automated Agilent 6890/5973 GC/MS system interfaced to an Entech 7100A cryogenic preconcentrator operated in the microscale purge-and-trap (MPT) mode. GC/MS analysis of volatile organic species generally followed the guidelines found in U.S. EPA Compendium Method TO-15 (EPA 1999) and more details of similar analyses are presented elsewhere (Cowen et al., 2008; MacGregor et al., 2008). A constant flow of helium was maintained at 1.2 mL/min through an Agilent J&W DB-1 (60 m x 0.32 mm, 1 μm film thickness) column. The oven temperature was programmed by first holding it at 35°C for 5 minutes, then increasing it at $6^{\circ}\text{C}/\text{min}$ to 150°C , followed by an increase of $15^{\circ}\text{C}/\text{min}$ to 220°C , where it remained for 6 minutes (total time 34.8 min). The mass spectrometer was operated in the full scan mode from m/z 25 to 300.

On each day that analyses were performed, a nominally hydrocarbon-free air blank was analyzed to ensure that the GC/MS was free of contamination. Typically, VOCs in the air blank are present at concentrations less than 0.2 parts per billion [ppb] by volume. The blank check was followed by analysis of a TO-15 calibration mixture containing 62 VOCs at either 2 or 10 ppb in air to check instrument calibration, retention times, and overall system performance. Three internal standard compounds (benzene-d₆, toluene-d₈, and chlorobenzene-d₅) were analyzed each at approximately 4.5 ppb along with each blank, standard, and headspace sample. Internal standard responses were used to track and correct for run-to-run variability in the performance of the cryogenic preconcentration system and in mass spectrometer detector response.

Headspace VOC concentrations were calculated by using relative response factors of one of two different surrogate compounds found in the VOC calibration mixture. (Relative response factors were scaled to the total ion current of the toluene-d₈ internal standard response.) Among other factors, the presence of oxygen in a VOC, along with its structure (whether it is aliphatic, aromatic, etc.), and its molecular weight affect the magnitude of its total ion current response in a mass spectrometer. The surrogates selected, 4-ethyl toluene and 2-hexanone, were chosen to represent the approximate mass spectral response of VOCs identified in the headspace samples that do not contain oxygen and those that do, respectively. Ethyl toluene is an aromatic hydrocarbon with a molecular weight and chemical structure similar to that of monoterpenes, whereas 2-hexanone is a carbonyl compound with some aliphatic character and a mid-range VOC molecular weight. In addition, these surrogates were selected because they did not coelute

with other compounds in the 62 component calibration mixture, thus allowing for the accurate measurement of their total ion current responses.

Excluding the three internal standards and obvious analytical artifacts (such as polymethylsiloxanes due to column or septum bleed), the top 20 peaks by total ion current area were selected from each sample chromatogram and tentatively identified by mass spectral library matches to compounds in the 2002 library from the National Institute of Standards and Technology. In general, the compound with the highest match probability was selected. Consistency of the proposed match's chemical structure and molecular weight with its observed retention time was also considered. In some cases, these considerations led to selecting a compound with a lower match probability and/or identifying compounds as one of a number of different possible isomers. For some products, fewer than 20 peaks were identified because peak areas fell either at or below a signal-to-noise ratio of approximately 3:1 or the mass spectral library searches were inconclusive. Compounds having estimated concentrations below 100 $\mu\text{g}/\text{m}^3$ were censored to ensure only a product's primary VOC emissions were reported.

To confirm that identification of the top 20 compounds by peak area produced robust results, alternative reporting thresholds were investigated, such as identifying the compounds comprising up to 99% of the total chromatographic peak area or identifying all compounds except those having areas less than 1% of the total chromatographic peak area. Reporting the top 20 peaks captured 95% of the total ion current chromatographic peak area for 19 of the 25 products. The alternative thresholds produced comparable results.

References:

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