



Indoor Air Analysis of Volatile Organic Compounds

Using Capillary Column Gas Chromatography/Mass Spectrometry

Office of Emergency and Remedial Response
Emergency Response Division
Environmental Response Branch MS-101

Quick Reference Fact Sheet

Introduction

The quality of indoor air and the resulting health risk associated with some potential exposure to volatile organic compounds (VOCs) from indoor air have become major concerns to building occupants, especially office workers. To effectively address these concerns, indoor air monitoring programs are needed which can produce data of known quality. The ensuing analytical method developed by the United States Environmental Protection Agency/Environmental Response Team (U.S. EPA/ERT), in conjunction with the Response Engineering and Analytical Contract (REAC), provides rapid turnaround of sample results while incorporating rigorous quality assurance/quality control (QA/QC) procedures to ensure reliability of the analytical data.

The gas chromatography/mass spectrometry (GC/MS) method was developed to provide support for the U.S. EPA/ERT indoor air quality program. The GC/MS method was designed to identify and quantify 45 target VOCs (i.e., aliphatic, aromatic, and chlorinated hydrocarbons) as well as identify non-target VOCs related to indoor air environments.

The Analytical Method

Multi-residue trace organic analyses for air samples are greatly dependent upon MS for unambiguous identification and confirmation of volatile and semi-volatile compounds. It is the preferred detection method because of limitations in selectivity of alternative micro-analytical techniques. The proposed indoor air method uses a full scan GC/MS and a fused silica capillary column for analyzing ambient air samples collected on charcoal tubes. The method was evaluated on charcoal tubes spiked with known quantities of 45 target VOCs and indoor air samples collected from office and home environments. It was also evaluated by determining desorption efficiencies, recovery studies, linearity range, method detection limits (MDLs), accuracy, and reproducibility. Identification and quantification of compounds tested were made by compar-

ing retention times and mass spectral data of unknown compounds with known compounds from calibration standards.

Materials - Stock standard solutions of 45 target VOCs were prepared by accurately weighing 500 ± 0.1 mg of each neat compound into a 25 mL volumetric flask and diluting to mark with benzene free carbon disulfide (CS_2). Working and daily standards were prepared by serial dilution of the 20 mg/mL standard mixture with CS_2 . Standard stock solutions of decafluorotriphenylphosphine (DFTPP) and isotopically labeled (cyclohexane- d_{12} , toluene- d_8 , 1,4-dichlorobenzene- d_4 , and naphthalene- d_8) internal standards (IS) were prepared at 10,000 $\mu\text{g/mL}$ each by weighing 100 ± 0.1 mg of DFTPP and IS into two separate 10 mL volumetric flasks and diluting to mark with dichloromethane and CS_2 , respectively. Secondary solution standards at 1000 $\mu\text{g/mL}$ were prepared from the stock solution by serial dilutions. The stock and secondary solutions were stored at -10°C to -20°C in Teflon®-lined crimp-top amber bottles.

Sample Collection - Air samples from home and office areas were collected on 600-mg two-stage charcoal tubes (400-mg front- and 200-mg back-activated charcoal separated with a foam plug) with Gillian monitoring pumps. A flow rate of 2 L/min (for a total of 1,200 L samples) was used throughout the study in order to achieve lower detection limits. The charcoal tubes were desorbed with 2 mL CS_2 spiking 1 mL of the sample extract with IS and analyzed by a capillary column GC/MS.

GC/MS System - The analytical system consisted of a HP5995A GC/MS equipped with an HP7673A autosampler and controlled by an HP-1000 RTE-6/VM computer data system equipped with the National Institute of Standards and Technology PBM Mass Spectral Library. A 30 m x 0.32 mm ID, Rtx-5 (Restek Corp.), fused silica capillary column with a 0.50 μm film thickness was used to separate the compounds tested. The analytical design was a totally automated system for sample injection, analysis, data reduction, and reporting.

Method with Acceptance Criteria

The QA/QC procedures are integral to analytical methods which produce data of known quality. The following guidelines were used prior to initiating on-going data collection, i.e., blanks, calibrating standards, or samples:

Tuning and Calibration - The GC/MS system was tuned daily or every 12 hours with 50 ng DFTPP. The results were then checked to verify that the U.S. EPA tuning and mass spectral ion abundance criteria were met. The system was initially calibrated with a standard VOC mixture in the concentration range of 1 µg/mL to 100 µg/mL (1, 5, 10, 25, 50, and 100 µg/mL) using the internal standard method; and was routinely checked by analyzing a continuing calibration standard (VOC mixture at 25 µg/mL with IS at 50 µg/mL) to ensure that the initial instrument sensitivity and linearity did not change significantly.

Acceptance Criteria - The data from the initial and continuing calibrations were used to calculate average relative response factors (RRF_i) and continuing relative response factors (RRF_c), respectively. For the calibration to be valid, a criteria of maximum percent relative standard deviation ($\%RSD \leq 30$) and a minimum $RRF_i \geq 0.2$ was adopted for all target compounds in the initial calibration. For the continuing calibration check, measured RRF_c must be within $\pm 20\%$ (i.e., $\%D \leq 20$) of the mean values calculated during initial calibration. In addition, all target compounds must have a minimum $RRF_c \geq 0.2$.

Desorption Efficiency (DE) - Desorption efficiency corrections were applied for each compound detected from samples analyzed. The DEs were determined for the method Target Compound List (TCL) at 2, 10, 50, and 200 µg levels and were established for every new lot of carbon for each compound before samples were analyzed.

Detection Limits, Accuracy, and Precision - The MDLs for the compounds tested were determined to be better than 0.2 parts-per-billion-by-volume (ppbv) at the 99 percent confidence level. The linearity of the GC/MS system (1 to 100 µg/µL) was demonstrated by the initial six point calibration data for the target compounds. The accuracy and reproducibility (precision) of the method, determined by analyzing a set of four replicate spikes at 50 µg level, was found to be better than 80 percent and 10 percent, respectively.

Applications

The indoor air method has been used for over five years to analyze ambient air samples from indoor (homes and offices) and outdoor (tire fires) environments. The results from an indoor air study in a northern New Jersey urban

office and site were compared with a VOC-INDO data base [a national data base comprised of 320 VOCs (with 66 VOCs measured indoors and 321 measured outdoors) from a distribution of volatile organic chemicals in indoor and outdoor air]. Nearly 90 percent of the indoor air data was from California and New Jersey. The outdoor air data was predominately from California, New Jersey, and Texas.

The range of results for individual compounds varied from not detected [$<MDL = 0.1$ ppbv] to less than 1.0 ppbv (indoor air) and 36.0 ppbv (outdoor air). The compounds normally detected are either in the background outdoor/urban air (1,1,1-trichloroethane, carbon tetrachloride, trichloroethene, etc.) or from automobile exhaust (benzene, toluene, and xylene).

Conclusions

The MDLs for the compounds tested were determined to be better than 0.2 ppbv at the 99 percent confidence level. The accuracy and reproducibility (precision) were better than 80 percent and 10 percent, respectively. The QA/QC procedures were found to be essential criteria for obtaining reliable analytical data. Based on over five years of experience using the proposed indoor air method with full scan GC/MS and fused silica capillary column, the following conclusions have been reached:

- The analytical results obtained are usually close to the method detection limit values.
- The method provided quality VOC data for indoor and outdoor air environments with quick turnaround (one day) for emergency response samples.
- The results indicate that 1, 1, 2, 2-tetrachloroethane may undergo in-situ degradation or reaction on charcoal tubes.
- The advantage of GC/MS over GC/FID detection is that a broad spectrum of target compounds can be unambiguously identified and quantified and non-target compounds identified as tentatively identified compounds (TICs).

Disclaimer

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