Quality Assurance of Real-Time VOC Measurements Using AROMA-VOC

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Abstract

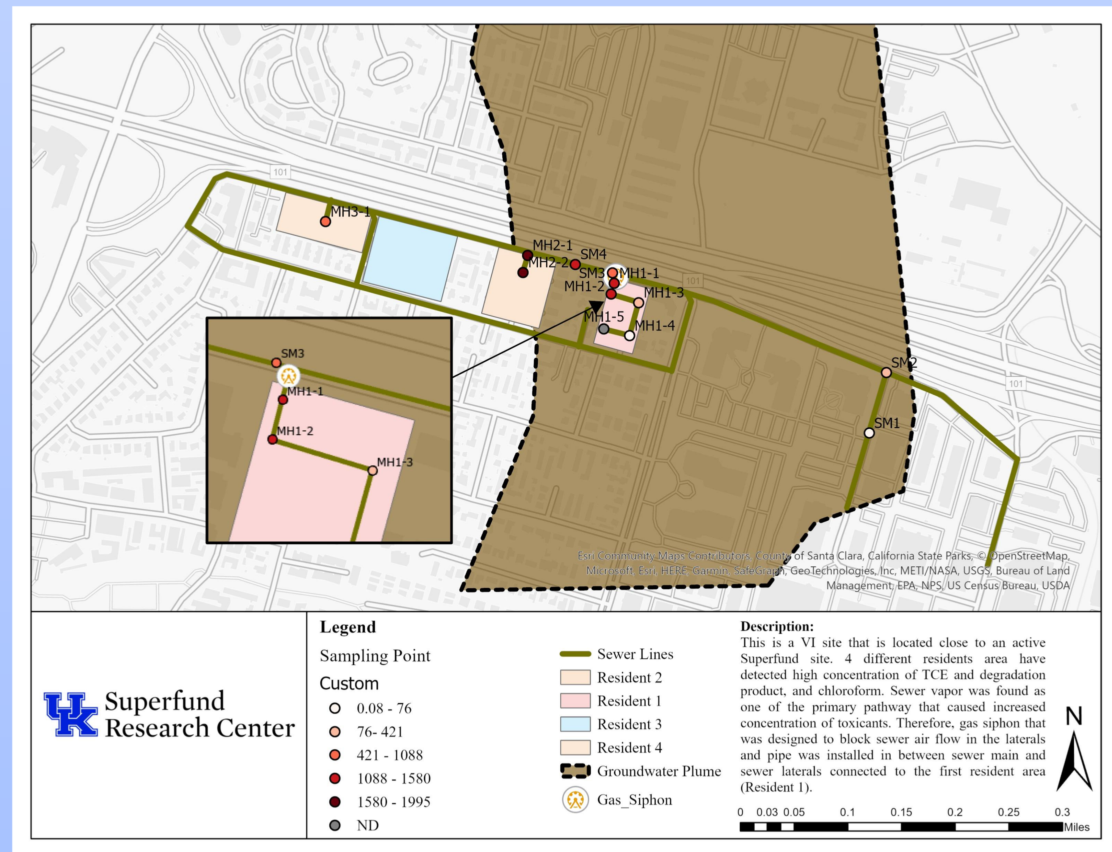
Vapor intrusion is a nationwide problem where foundation cracks and building slab imperfections have long been considered as primary intrusion pathways into indoor spaces. More recently, sewer connections and other building infrastructure connections have been shown to increase the potential for vapor intrusion at a site. These is a need for improved characterization techniques, including real-time monitoring of chemical concentrations in these complicated transport pathways. A range of sampling techniques and analytical methods (e.g. TO-15A, passive sampling, real-time monitoring, etc.) are used at sites depending on different environmental conditions and site assessment needs. Real-time chemical monitoring provides considerable advantages and is the focus of this research. In the present work, a Quality Assurance Project Plan (QAPP) is developed for a real-time vapor phase analytical instrument, AROMA-VOC. AROMA-VOC is manufactured by Entanglement and detects concentrations of volatile organic compounds (VOCS) within parts-per-billion (ppb) and parts-per-trillion (ppt) range. The core of the instrument uses technology of Cavity Ringdown Spectroscopy coupled with Thermal Desorption to identify and quantify chemical concentrations of interest. This technology provides an alternative to other real-time devices (e.g. GC/MS), but performance specifics of instrument has not be well-described. The QAPP describes the sensitivity and intensity of the instrument. Calibration curves of the instrument been generated in this study. AROMA-VOC exhibits high repeatability of calibration curves for 8 different chemicals with r-squared values higher than 0.98. The r-squared values have demonstrated the method used to generate samples and analyzed samples producing consistent errors. A series of parameters are established, including precision, trueness, recovery, specificity, Limit of Detection (LOD), etc. The framework of the project plan will be similar to US Environment Protection Agency (US EPA) established QAPP.

AROMA-VOC, Pennell Lab at University of Kentucky

Background

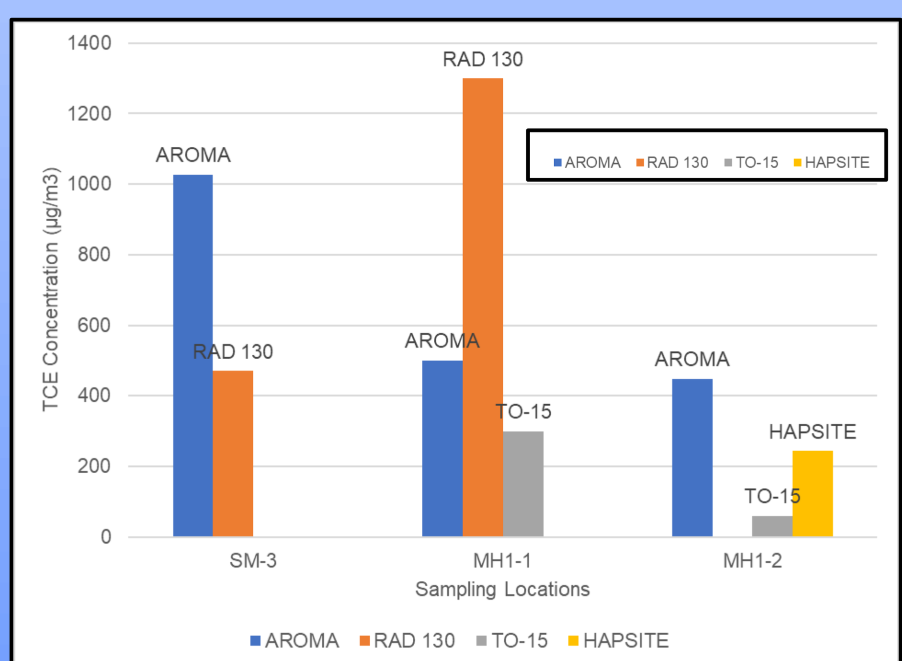
Real-time VOC monitoring technology has been a scare and necessary resource as part of vapor intrusion assessment and mitigation. One rare and costly technique is the EPA Trace Atmospheric Gas Analyzer (TAGA) (see photo to right), which helped to establish the benefit of real-time VOC monitoring. A more commonly used real-time technique is the HAPSITE, which requires a skilled technician who can recalibrate and troubleshoot in the field (see photo below). In 2018, AROMA-VOC was developed by Entanglement Technologies, Inc. in 2018 as a new real-time monitoring device with the intent of being easier to use and more accessible than alternatives.

Trace Atmospheric Gas Analyzer Frazier (2023)



HAPSITE® KD Analytical (2023)

At many hazardous sites, various sampling and analysis approaches are used. Because of this variability, it is important that methods for sampling/analysis are reliable and accurate. For example, VOC sampling at the site above included real-time monitoring analyzers used to collect on-site concentration data while the rest rely on established sampling method (e.g. TO-15 & TO-17) and certified laboratory for analysis (data to right).



Purpose and Methods

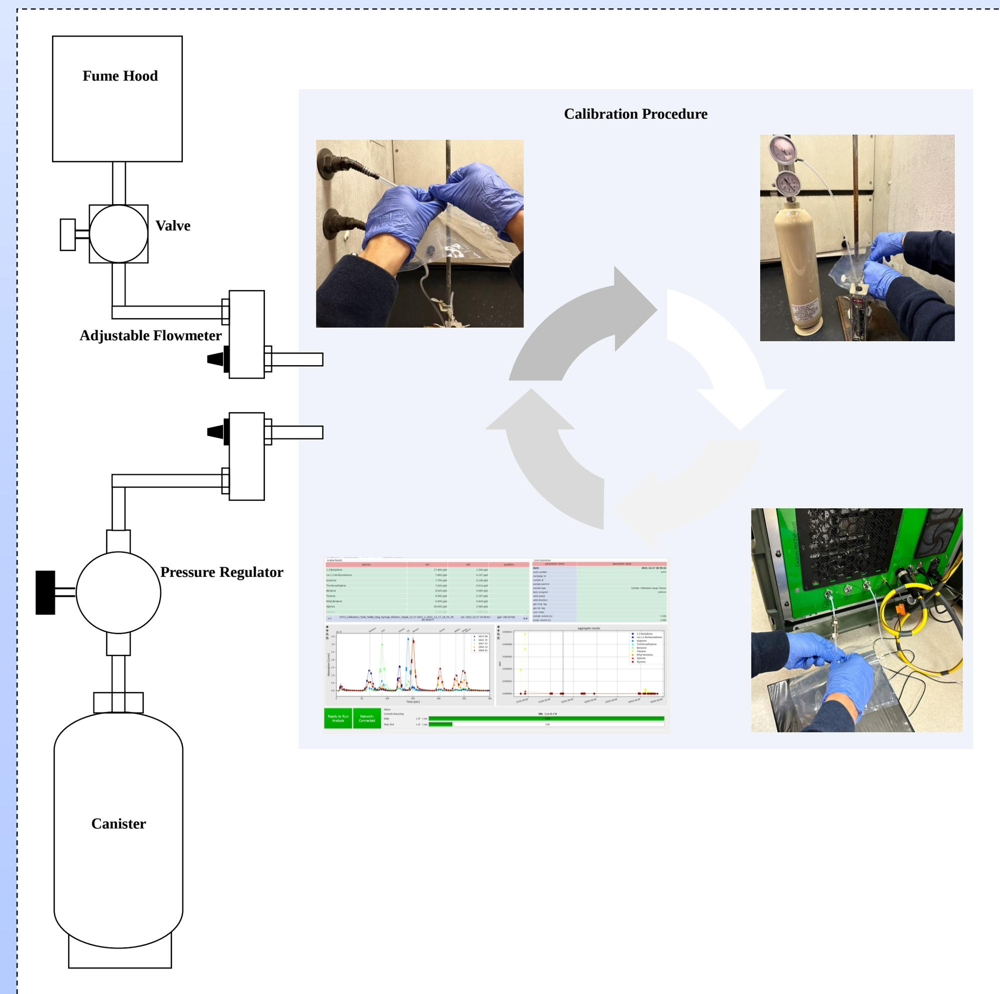
To date, the performance and sensitivity of the AROMA-VOC instrument have not been systematically investigated. There is no scientific publication record of the reliability or the accuracy. This research develops Quality Assurance criteria for AROMA-VOC.

QUALITY ASSURANCE PROCEDURES

Criteria	Definition	Expressions and Requirements	Procedure	References
1. Accuracy/ Precision	The closeness of agreement between independent test results obtained under stipulated conditions.	N/A	N/A	N/A
1.1 Repeatability Precision	Precision under conditions where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time.	**$r = 2.83 \times SD_r$;** r: repeatability limit; SD: standard deviation of measurements **$RSD_r = 100 * SD_r / \bar{x}$;** RSD_r: relative standard deviation; $\bar{X}$: mean of measurements Calculated RSD_r should be 0.5-0.6 times theoretical values determined by **Horwitz function = 2 exp (1-0.5logC)**; C: concentration of analyte Compare %RSD with "Table 4" below.	Prepare and analyze samples with 5 different concentrations (10,7,5,3,0 ppb) in a Teflon bag with constant volume. Repeat each concentration 3 times.	[1, 2]

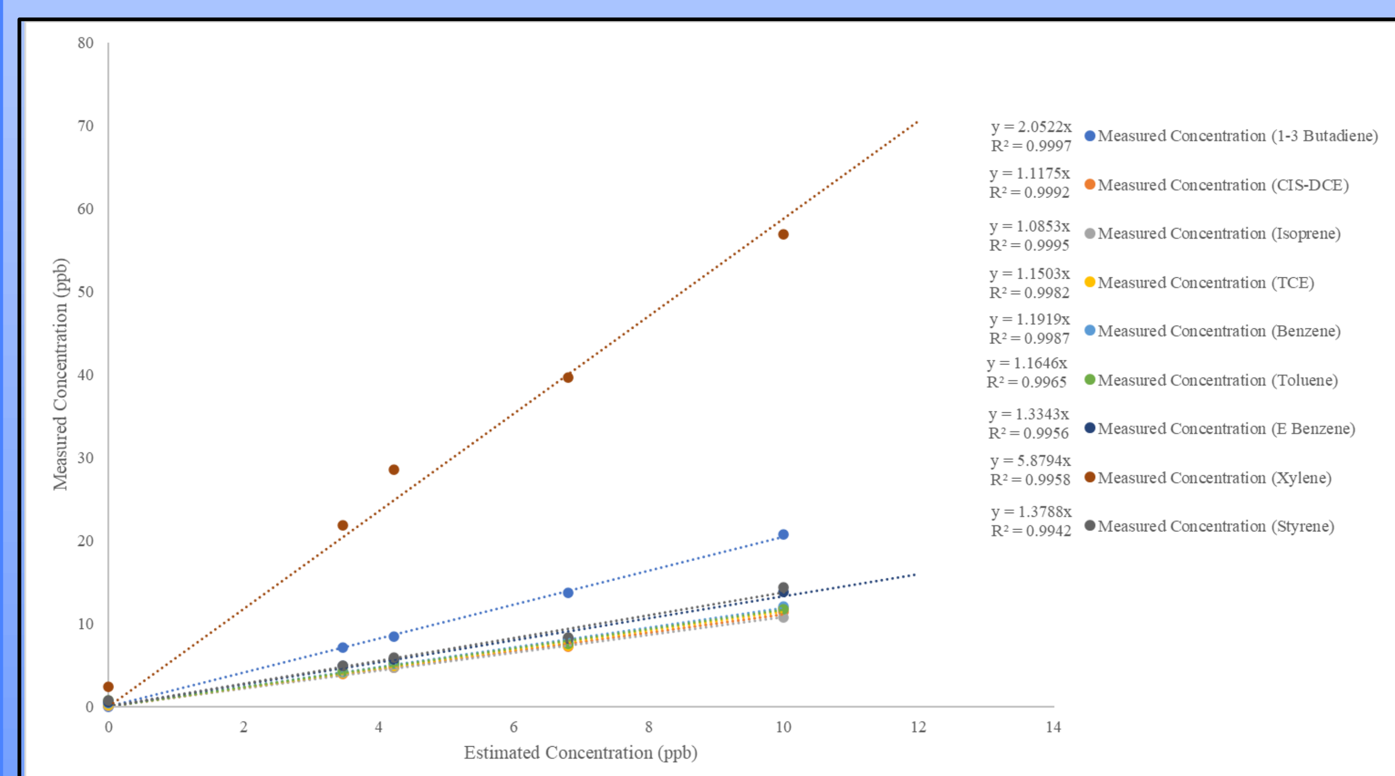
QUALITY ASSURANCE PROCEDURES (CONT.)

Criteria	Definition	Expressions and Requirements	Procedure	References
2. Trueness	The closeness of agreement between the expectation of the test result (expected mean value) and an accepted reference value (true value).	If Certified Reference Materials (CRMs) are used: **Bias = % error**: difference between measured value and true value $Z-score = \frac{X_{found} - X_{certified}}{\sqrt[2]{\frac{SD_{found}}{n_{found}} + \left(\frac{SD_{certified}}{n_{certified}}\right)^2}}$ **Z-score ≤ 2**	Same as above. Compare measured concentration with true concentration. Calculate z-score	[1]
3. Recovery	The fraction of analyte added to the test sample	**%recovery = 100*[$spike_{matrix\ sample}$/$spike_{blank}$]**	Choose a spike concentration (e.g., 1 or 3 ppb)	[1, 3]



Preliminary Results (manuscript with QA/QC FORTHCOMING)

Nine VOCs are calibrated using AROMA-VOC using standard produced by Apel-Riemer Environmental Inc. Standard. The standard gas is certified at 10ppb concentration. Trendlines for each of the chemical compounds have r-squared above 0.995.



Future Experiments

Results obtained for AROMA-VOC will be compared the industry standard (GC/MS).

Volatile Compound	Precisions: Repeatability (%RSD)	Precisions: Intermediate (%RSD)	Precisions: Reproducibility (%RSD)	Specificity: FP[1] (%)	Specificity: FN[2] (%)	LOD[3] (μg/L)	LOQ[4] (μg/L)	Recovery (%)
AROMA-VOC								
1,3-Butadiene								
Benzene								
Cis-1,2-dichloroethene								
Ethyl Benzene								
Isoprene								
Toluene								
Trichloroethylene								
Styrene								
Xylene								
GC-MS[5]								
1,3-Butadiene	4.91 @ 5 μg/L		5.95 @ 5 μg/L			0.025	0.083	93.8
Benzene	1.85 @ 5 μg/L		2.41 @ 5 μg/L			0.019	0.065	92.5
Cis-1,2-dichloroethene	-		-			-	-	-
Ethyl Benzene	1.76 @ 5 μg/L		5.13 @ 5 μg/L			0.015	0.05	92.7
Isoprene	-		-			-	-	-
Toluene	1.90 @ 5 μg/L		5.10 @ 5 μg/L			0.017	0.058	94.0
Trichloroethylene	2.28 @ 5 μg/L		3.83 @ 5 μg/L			0.027	0.091	91.9
Styrene	2.14 @ 5 μg/L		2.45 @ 5 μg/L			0.014	0.047	82.6
Xylene	3.49 @ 5 μg/L		2.98 @ 5 μg/L			0.021	0.071	95.9

Volatile Compound	GC-MS[1] Certified Value (μg/L)	GC-MS[1] Measured Value (μg/L)	GC-MS[1] Recovery (%)	GC-MS[1] Z-score	AROMA-VOC Certified Value (μg/L)	AROMA-VOC Measured Value (μg/L)	AROMA-VOC Recovery (%)	AROMA-VOC Z-score
Benzene	17.0	18.68 ± 0.33	109.9	0.729				
1,3-Butadiene	<4.3	0.06 ± 0.01	-	0.258				
Cis-1,2-dichloroethene	-	-	-	-				
Ethyl Benzene	19.4	19.98 ± 0.31	103.0	-				
Isoprene	-	-	-	-				
Toluene	11.0	11.04 ± 0.19	100.4	0.19				
Trichloroethylene	75.2	80.59 ± 1.71	107.2	0.796				
Styrene	40.8	35.58 ± 0.32	87.9	-				
Xylene	21.0	20.50 ± 0.19	97.6	0.745				

Volatile Compound	GC-MS[1] Calibration Curve Equation	GC-MS[1] Linearity (R^2)	AROMA-VOC Calibration Curve Equation	AROMA-VOC Linearity (R^2)
1,3-Butadiene	y = 16910x + 2436.6	0.9994		
Benzene	y = 75303x + 9609.7	0.9997		
Cis-1,2-dichloroethene	-	-		
Ethyl Benzene	y = 121781x + 6841.1	0.9999		
Isoprene	-	-		
Toluene	y = 97609x + 97944	0.9996		
Trichloroethylene	y = 24918x – 6931.5	0.9990		
Styrene	y = 57766x – 10087	0.9999		
Xylene	y = 93040x – 2895.5	0.9998		

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