Urine Odors in an Urban Dwelling

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Odor Assessment with an Electronic Nose

Conventional odor assessment methods use subjective human panels to evaluate ambient air samples collected in tedlar bags. A summary report using common descriptors such as foul, sweet, pungent, etc. is produced. These reports are useful but difficult to interpret and are certainly not quantitative. Electronic noses (eNoses) using an array of dissimilar but not specific chemical sensors can also be used to evaluate odors by simulating the human olfactory system. However, physical sensors have limited performance because of overlapping responses and hence cannot separate or quantify odor chemistry.

A new type of electronic nose, called the zNose®, is based upon ultra-fast gas chromatography, simulates an almost unlimited number of specific virtual chemical sensors, and produces olfactory images based upon aroma chemistry. The zNose® is able to perform analytical measurements of volatile organic vapors and odors in near real time with part-per-trillion sensitivity. Separation and quantification of the individual chemicals within an odor is performed in seconds. An integrated vapor preconcentrator coupled with the electronically variable detector, allow the instrument to measure vapor concentrations spanning 6+ orders of magnitude. In this report a portable zNose®, shown in Figure 1, is used to assess urine odors found in an urban dwelling and to quantify the concentration of chemicals in these odors.

Figure 1- Portable zNose® gas chromatograph.

How the zNose™ Quantifies the Chemistry of Odors

A simplified diagram of the zNose™ system shown in Figure 2 consists of two parts. One section uses helium gas, a capillary tube (GC column) and a solid-state detector. The other section consists of a heated inlet and pump, which samples ambient air. Linking the two sections is a "loop" trap, which acts as a preconcentrator when placed in the air section (sample position) and as an injector when placed in the helium section (inject position). Operation is a two step process. Ambient air (aroma) is first sampled and organic vapors collected (preconcentrated) on the trap. After sampling the trap is switched into the helium section where the collected organic compounds are injected into the helium gas. The organic compounds pass through a capillary column with different velocities and thus individual chemicals exit the column at characteristic times. As they exit the column they are detected and quantified by a solid state detector.

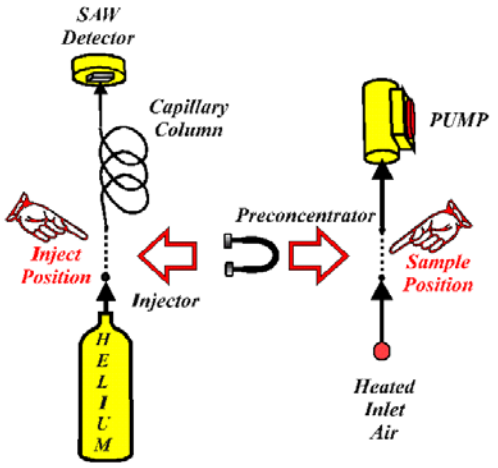

Figure 2- Simplified diagram of the zNose™ showing an air section on the right and a helium section on the left. A loop trap preconcentrates organics from ambient air in the sample position.

An internal high-speed gate array microprocessor controls the taking of sensor data which is transferred to a user interface or computer using an RS-232 or USB connection. Calibration is accomplished using a single n-alkane vapor standard. A library of retention times of known chemicals indexed to the n-alkane response (Kovats indices) allows for machine independent measurement and compound identification. The time derivative of the sensor spectrum yields the spectrum of column flux, commonly referred to as a chromatogram. The chromatogram response (Figure 3) of n-alkane vapors (C6 to C14) provides an accurate measure of retention times. Graphically defined regions shown as red bands calibrate the system and provide a reference time base against which subsequent chemical responses are compared or indexed. As an example, a response midway between C10 and C11 would have a retention time index of 1050.

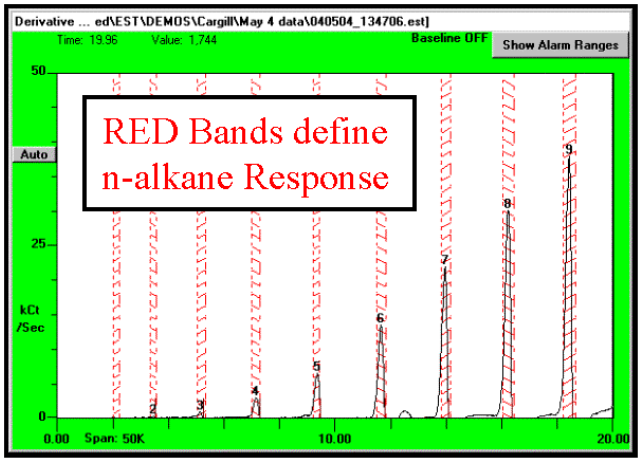

Figure 3 - Chromatogram of n-alkane vapors C6 to C14).

Urine Odor Standards

Odors from fresh and 'old' urine samples were measured and compared. The 'old' urine was obtained from bottles left in the attic of the dwelling and was estimated to be over 1 year old. Approximately 10 milliliters of urine was placed in a septa-sealed 40 milliliter vials and allowed to equilibrate for 10 minutes at room temperature before the headspace vapors were tested using the zNose®. Vertically offset chromatograms of headspace measurements are shown in Figure 3. Approximately 14 distinct chemicals were detected and named according to their Kovats indices.

1	547	7.900	urine 546
2	600	8.000	urine 600
3	679	5.900	urine 662
4	785	4.461	urine 776
5	888	2.500	urine 888
6	972	2.377	urine 957
7	1016	2.067	urine 1009
8	1052	1.803	urine 1057
9	1080	0.900	urine 1081
10	1136	1.804	urine 1121
11	1197	1.900	urine 1196
12	1239	1.500	urine 1235
13	1315	1.699	urine 1315
14	1407	1.400	urine 1410

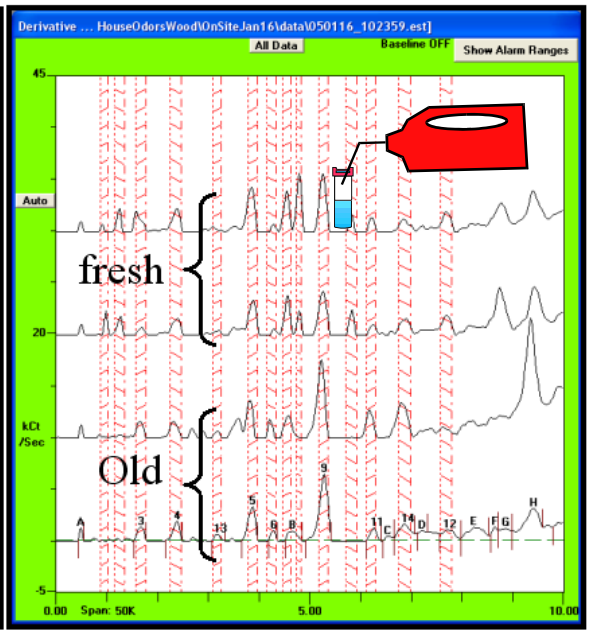

Figure 3- Replicate chromatograms of headspace vapors from fresh and old urine samples.

Differences between old and fresh urine odors can be more easily seen in the over-laid chromatograms of Figure 4. Older urine loses many of the more volatile compounds with indices below 650. In addition some of the mid range compounds (urine 1057, urine 1081 and urine 1196) are metabolized by bacteria and no longer present in old urine. In spite of these differences many of the major chemicals in urine odors remain unchanged over long periods of time.

Although not directly identified many of the volatile and odoriferous compounds in urine are known to be amino acids. This can be deduced from the comparison headspace measurements of Figure 5 where headspace vapors from a single drop of fresh blood are compared with headspace vapors from urine.

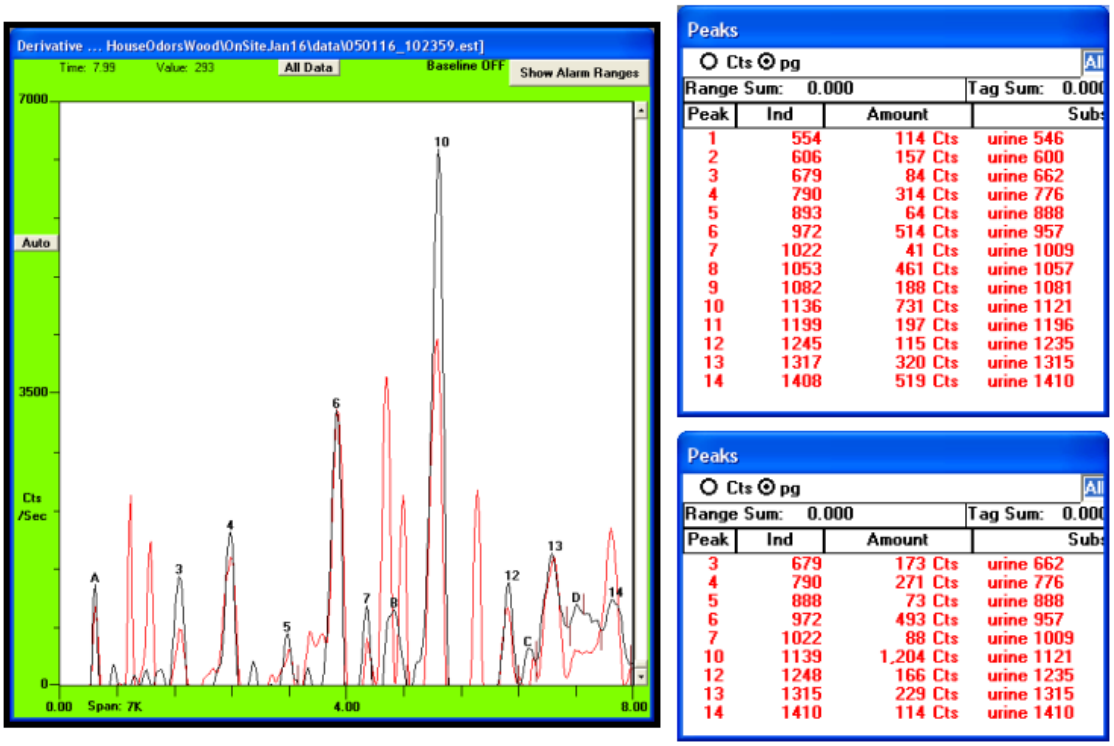

Figure 4- Overlaid chromatograms and peak area counts of headspace vapors from old and fresh (shown in RED) urine.

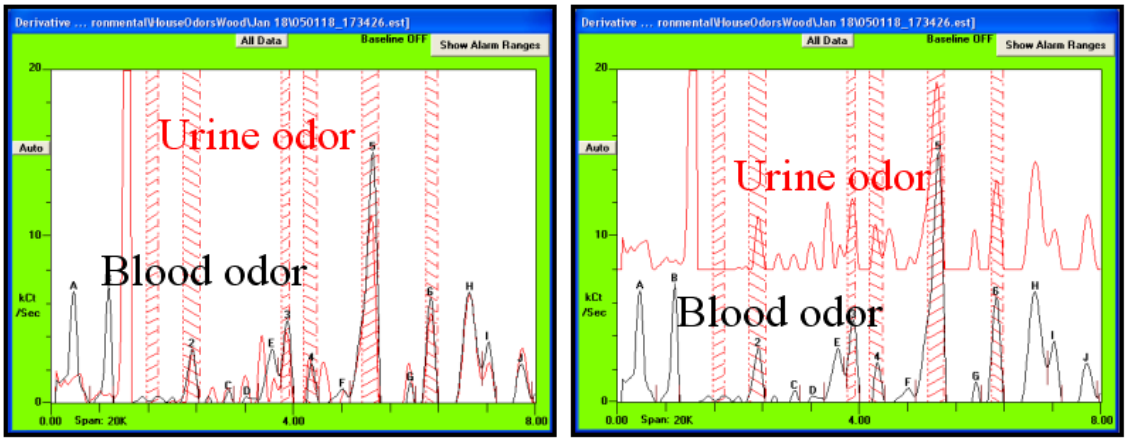

Figure 5- Offset and overlaid chromatograms of headspace vapors from blood and urine (shown in RED) show many of the same peaks since both contain amino acids.

The graphically defined bands shown in Figures 3 and 5 are used to define regions of retention time or retention indices specific to urine odors. Once defined, each region will acts as a virtual chemical sensor specific to an organic compound with a specific retention index. Alarm levels may be set for each virtual sensor in an array of sensors and the array aggregate response then defines the target odor of urine.

Description of On-Site Testing and Findings

The objective was to test ambient air within an un-inhabited house using the target odor profile of urine. The house was a large single story dwelling with over 14,00 square feet and contained many rooms as shown in the floor plan of Figure 6. No furnishings or personal belongings were present. Outside air and ambient air within the house was

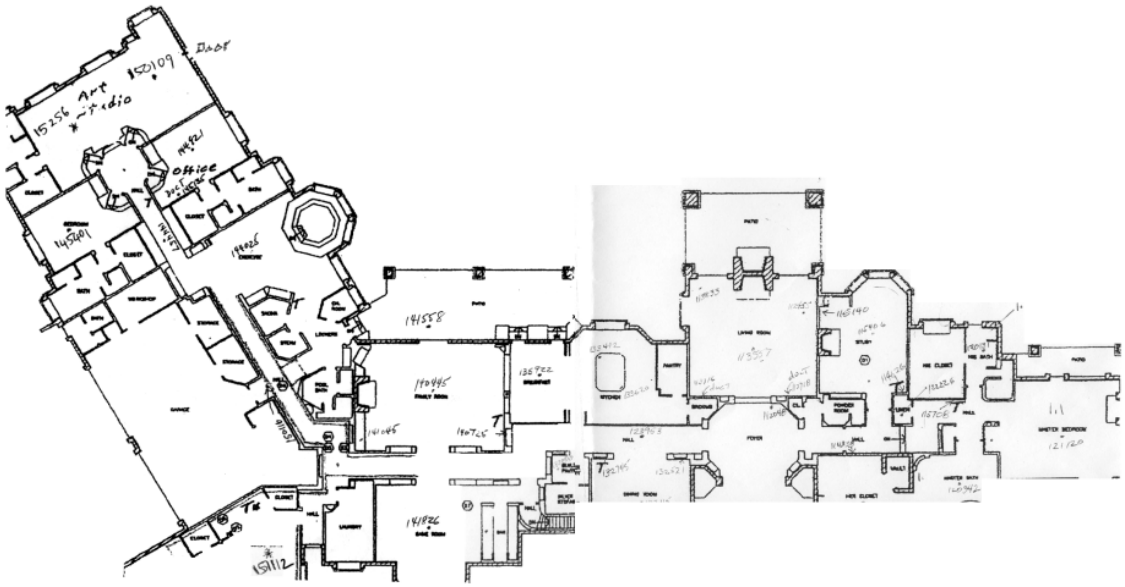

Figure 6- Floor plan of house in which ambient air was tested for traces of urine.

measured by a portable gas chromatograph (GC) and air preconcentrator. The preconcentrated air sample volume was 15 milliliters and the minimum detection level of the GC sensor was approximately 10 picograms. For all vapor samples tested the column (a db624) was temperature programmed to rise from 40^{o}C to 160^{o}C at 10^{o}C/second and data acquisition (chromatogram) time was 20 seconds. A detector temperature of 10^{o}C was used. With these instrument settings, the resultant detection levels for volatile organic compounds (C4 to C18) in air were in the low ppb range.

Ambient air throughout the house was evaluated by testing in several locations within each room as well as within air ducts where covers had been removed. Over 150 ambient air measurements were performed within the house (on site) as well as grab-samples at an off-site laboratory. In general trace levels (ppt to low ppb) concentrations of organic compounds specific to urine were detected throughout the house. A portion of the more than 150 measurements is shown using vertically offset chromatograms in Figure 7. Hatched red bands delineate compounds specific to urine odors and numbered peaks indicate urine compounds above an arbitrary threshold level of 20 counts.

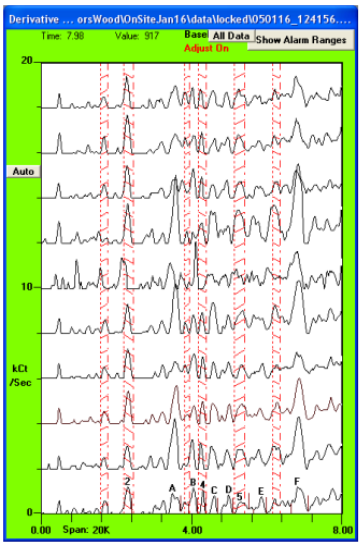

Figure 8-Typical measurements vertically offset for viewing. 10^{o} detector, 30 second sample, 10ps2a1b method, 140^{o}C valve, and 200^{o}C inlet

In bathrooms where toilets had been removed emissions from sewer pipes were tested as potential emission sources. As an example, in Figure 8 sewer pipe odor (cover removed) is compared with surrounding room air. The concentrations of targeted compounds within the sewer pipe were higher when the pipe cover was removed but did not appear to be a source of emissions when covered.

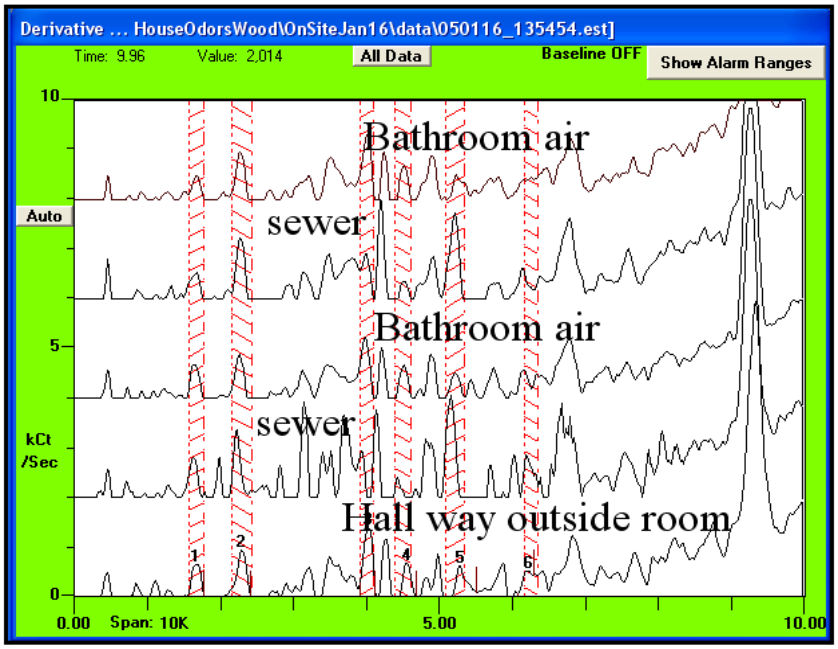

Figure 7 -Sewer odors in bathroom by butler's pantry 10^{o} detector, 30-second sample, 10ps2a1b method, 140^{o}C valve, and 200^{o}C inlet

In general, on-site testing did not reveal or detect any localized high concentration sources of odor emission in any rooms of the house. Instead there appeared to a general presence of urine odor throughout the house. As an example, ambient air tested in the hallway leading to the master bedroom clearly shows the presence of the same organic compounds found in urine when compared with offset chromatograms.

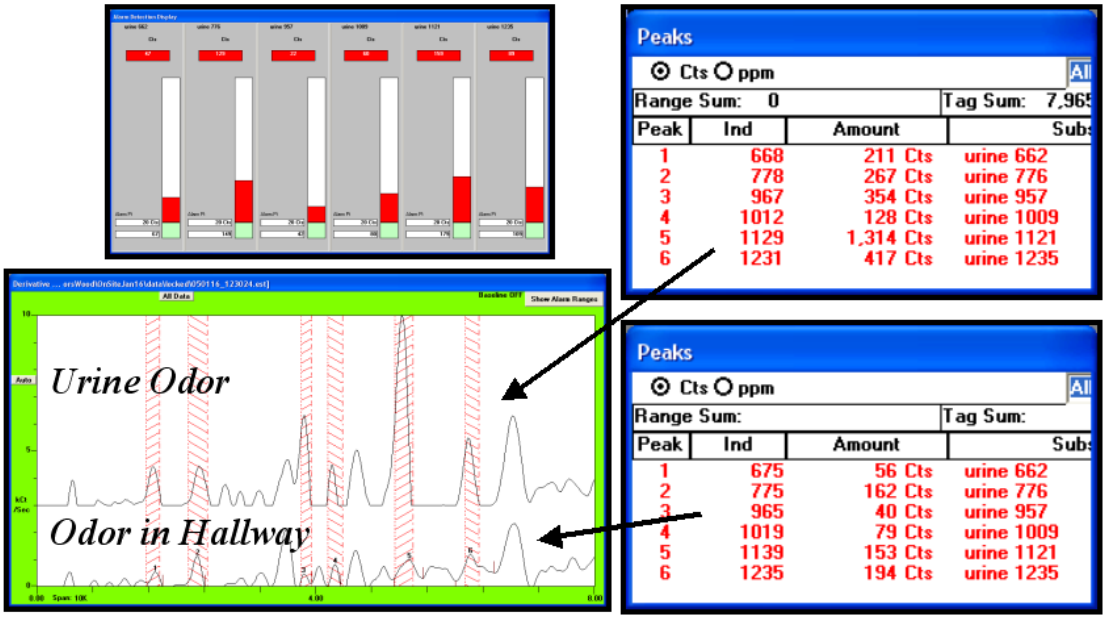

Figure 9- Odors in hallway leading to master bedroom. 10^{o}detector, 30-second sample, 10ps2a1b method, 140^{o}C valve, and 200^{o}C inlet

Other sources of organic compounds, which were investigated at the site, were fertilizers that had been used on the surrounding landscape and shrubbery. Odors from Turf fertilizer and Kelate powder, shown in Figures 10 and 11, were compared with odor from urine as well as the outside air surrounding the house. These fertilizers did show trace amounts of the same organic compounds found in urine. However, because their odor profile or signature was dominated by other high concentration organic compounds not detected in air outside or inside of the house, they were ruled out as the source of urine odors in the house.

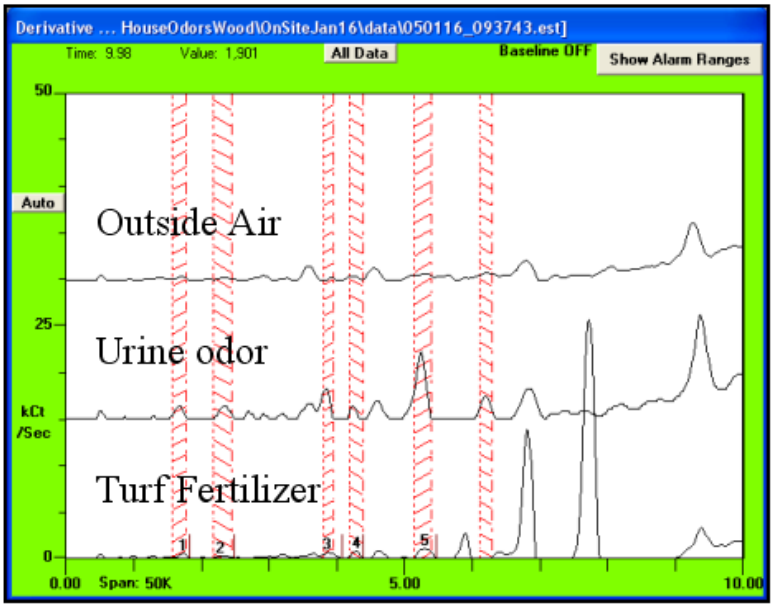

Figure 10- Turf fertilizer odor compared with urine and outside air measurements. 10^{o}detector, 30 second sample, 10ps2a1b method, 140^{o}C valve, and 200^{o}C inlet

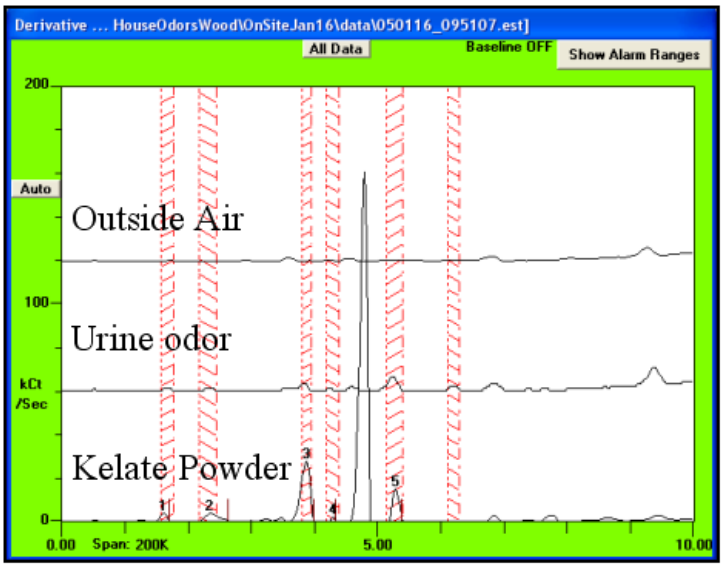

Figure 11- Kelate powder compared with urine and outside air measurements. 10^{o}detector, 30 second sample, 10ps2a1b method, 140^{o}C valve, and 200^{o}C inlet

Odors from drywall and insulation collected at the site (living room air duct) were investigated by placing samples in septa-sealed vials and directly sampling vapors thru a side-ported needle. Odors from comparable insulation and drywall materials from a California building (EST) were also tested and all were compared to urine odor, which is

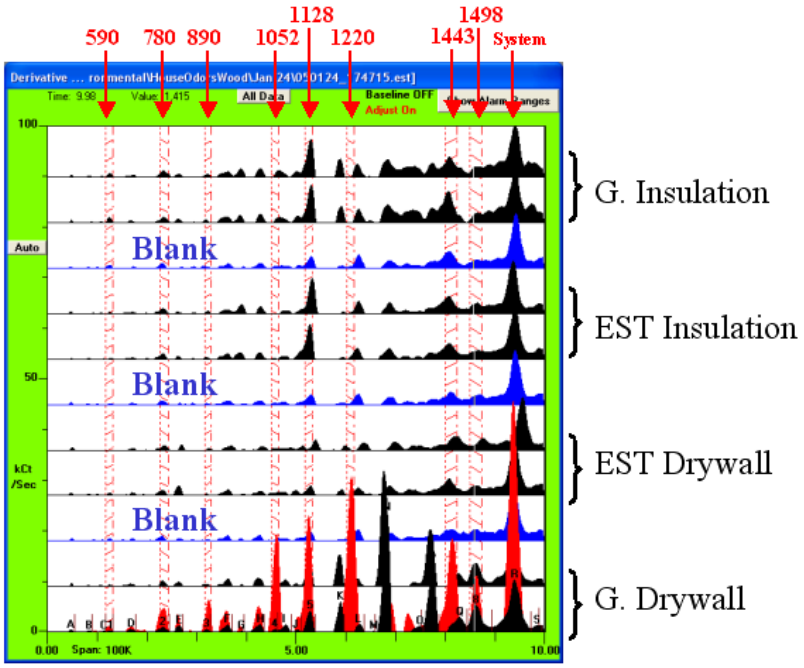

Figure 12- Odor s from insulation and drywall taken from dining room air duct. 10^{o}detector, 30 second sample, 10ps2a1b method, 140^{o}C valve, and 200^{o}C inlet

shown overlaid in red in Figure 12. Also shown in blue are odors from empty vials (blanks). The major peaks relevant to urine odors are shown as hatched bands and their indices shown at the top of the figure. Background peaks can be seen in the blank runs and are believed due to ambient air or sample needle carryover. The concentration of vapors from these samples was very low (ppt levels) and carryover and contamination made measurements difficult. Nevertheless, peaks 1220 and 1498 are of noteworthy because they only appeared in urine odors. Based upon this the insulation and drywall samples taken from the dining room duct appears not to be contaminated with urine.

To improve signal to noise in sample and ambient air vapor measurements a high flow vapor preconcentration step was implemented. In this technique vapors from samples are first preconcentrated in a metal tube filled with tenax (SKC) using a high sampling airflow, typically 450 ccm. After preconcentration the metal tube is inserted into the GC inlet and trapped vapors released into the instrument by heating the tube to 220^{o}C. The zNose® is designed to accommodate metal desorbtion tubes and by this technique is able to increase the sensitivity of ambient air measurements by many orders of magnitude.

High airflow sampling vapors from urine contaminated wood shavings (bagged samples in garage) were placed in a septa-sealed vial and equilibrated for 10 minutes before headspace vapors were tested. Headspace chromatogram results for sample No. 68332 are shown in the bottom trace of Figure 13. Four vertically offset chromatograms from urine are shown for comparison. The appearance of peaks at indices of 1220 and 1498 strongly suggest that this wood sample was contaminated with urine.

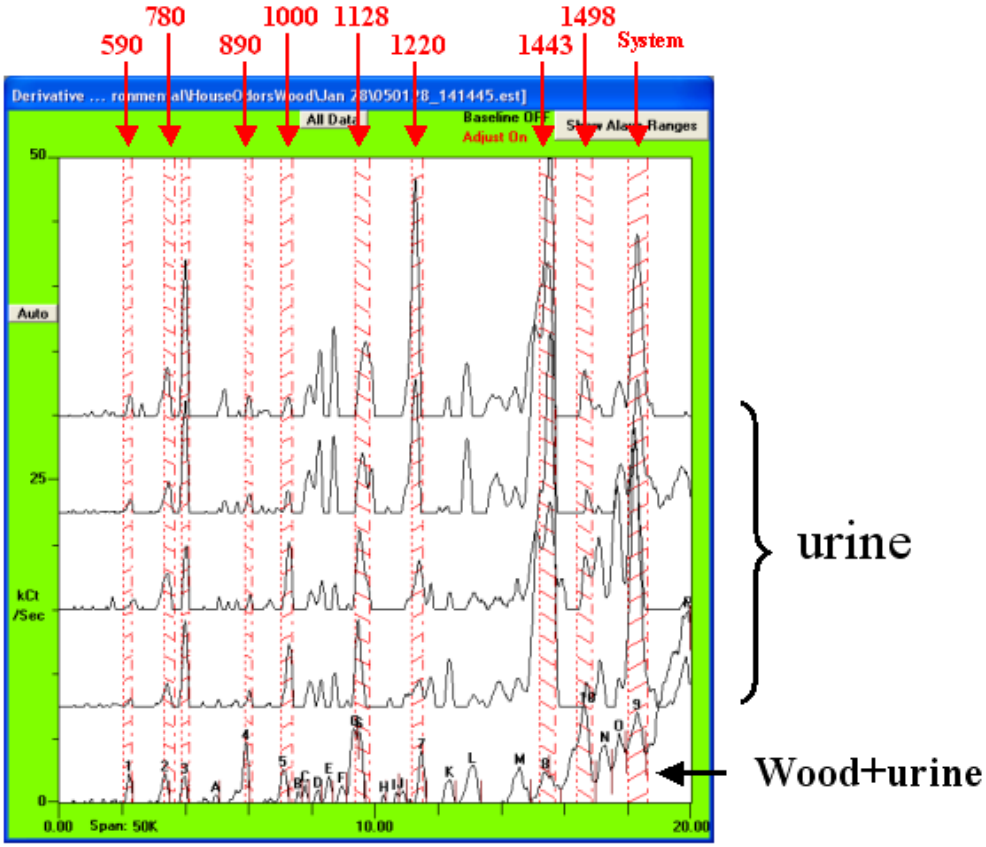

Figure 13- Odors from wood sample No. 68332 compared with urine odor. 20°detector, 2 min sample 450 ccm into tenax preconcentrator, 220°C desorber, 5ps2a1b method.

Although screening with a fast GC may indicate urine contamination this conclusion should be supported by independent laboratory testing with a GC/MS and by identification of the target compounds. The large numbers of compounds detected at ppt concentration levels, make independent confirmation imperative. The peak with index of 1498 is postulated to be phenylacetic acid, which is a common metabolite released in urine, and which has an odor described as sweet urine. Because of its high boiling point, 265°C, it would be difficult to remove by ventilation and readily adhere to surfaces. Many other metabolic compounds are present in urine and even more may be created over time as a result of bacteria present in the ambient environment.

Odors from samples of insulation taken from the dining room air duct were re-tested using a high flow preconcentrator and the results are shown in Figure 14 and compared with EST insulation samples and urine odor. The insulation does not appear to be contaminated with urine since the two peaks 1220 and 1498 are not present.

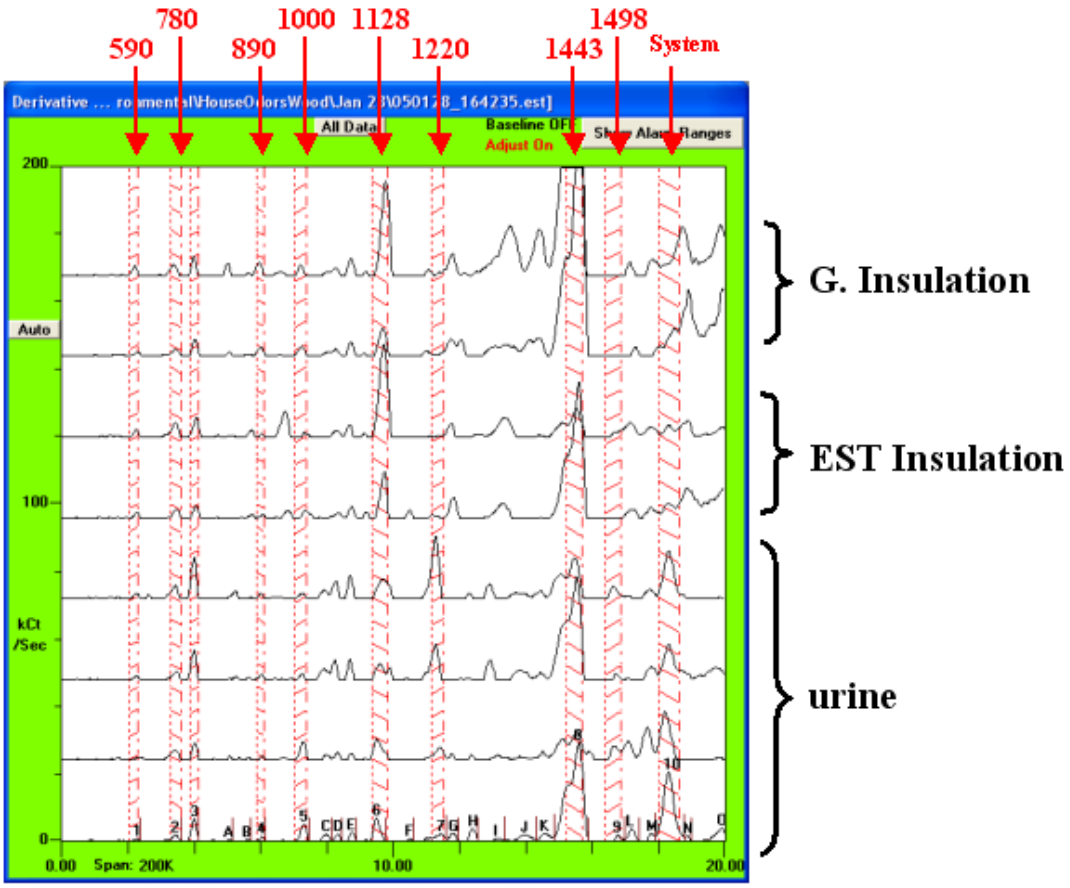

Figure 14- Odors from Wool Insulation compared with urine odor. 20° detector, 2 min sample 450 ccm into tenax preconcentrator, 220°C desorber, 5ps2a1b method.

Odors from samples of drywall taken from the dining room air duct were also re-tested using a high flow preconcentrator and the results are shown in Figure 15 and compared with EST drywall samples and urine odor. Interference from background is very low as seen in the blank chromatogram (in red) from preconcentration of vapors in an empty vial. The drywall does not appear to be contaminated with urine since the two peaks 1220 and 1498 are not present.

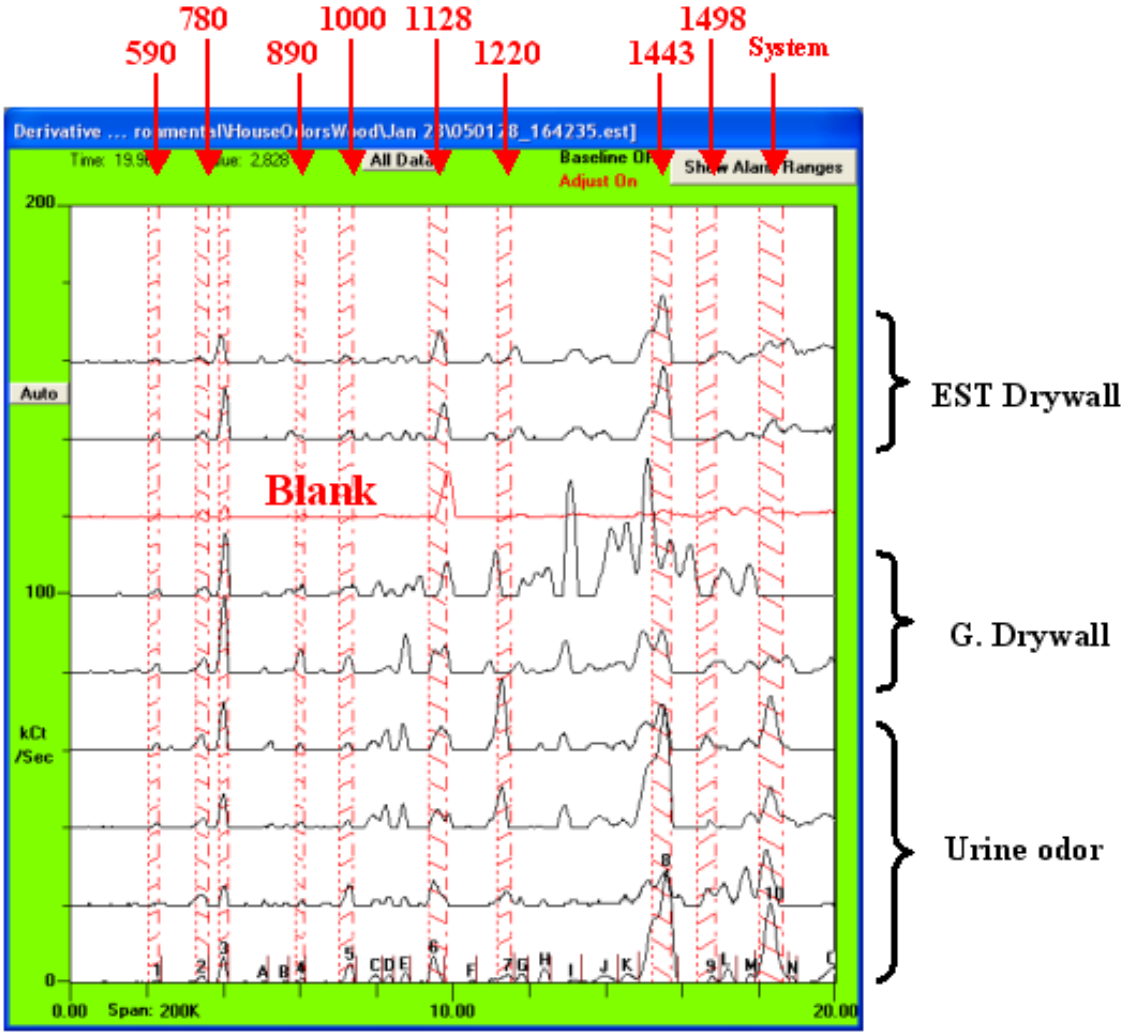

Figure 15- Odors from wallboard sample compared with urine odor.20^{o}detector, 2 min sample 450 ccm into tenax preconcentrator, 220^{o}C desorber, 5ps2a1b method.

Conclusions and Recommendations

Chemical profiling of urban indoor air can be performed on-site and in near real time using an ultra high speed portable gas chromatograph. It is possible to quantitively measure air quality on-site and to recognize the chemical signature of nusiance odors. Indexing of retention times for target compounds using an n-alkane vapor standard provides a convenient method of screening for target compounds. GC testing of ambient air coupled with sensory data from humans yields a more objective method of classifying and quantifying odors.

Results of testing an urban dwelling for the presence of organic compounds associated with urine odors have shown that these odors exist within the indoor air of the dwelling. Ambient air throughout the dwelling was evaluated by testing in multiple locations within each room as well as within air ducts. Over 150 ambient air measurements were performed within the house (on site) and grab-samples were also tested at an off-site laboratory. In general the concentration of organic compounds found was extremely low (ppt to low ppb) concentrations and chromatogram peaks also detected in urine vapors were detected in ambient air within the house. In bathrooms where toilets had been removed emissions from sewer pipes were tested as potential emission sources. The concentrations of targeted compounds within the sewer pipes were low and did not appear to be a source of odors within the house. However, because of the large numbers of background peaks at these low concentration levels it is difficult to be certain the peaks were actually metabolic compounds from urine without independent validation.

Other sources of organic compounds, investigated at the site were fertilizers that had been used on the surrounding landscape and shrubbery. Fertilizers did show trace amounts of the same organic compounds found in urine but their odor profile or chemical signature was dominated by other high concentration organic compounds, which were not detected in air outside or inside of the house. Odors from wood, which had been removed from the house and stored in the garage, tested positive for urine contamination. Insulation and drywall samples from the living room air duct did not show urine contamination.

Recommendations:

1. Collection and testing of high volume air samples from within the house using tenax absorption tubes. Split samples would allow independent validation.
2. Implement on-site testing protocol for measuring the concentration of targeted organic compounds in ambient air within the house.
3. Determination of acceptable target compound concentration levels for remediation.

The zNose® is a new tool which provides environmental and remediation engineers the speed, portability, precision, and accuracy needed for cost-effective on-site odor measurements. Such measurements, because they are based upon well known chromatographic methods, can easily be validated by independent laboratory testing. Acceptable odor levels, determined by trained sensory panels, can be used to validate remediation efforts by objective and quantitative on-site testing.