

# Forensic Evaluation of Soils for Presence of Decaying Flesh

## Final Report

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# Forensic Evaluation of Soils for Presence of Decaying Flesh

## I. Introduction

### I.1 Forensic Searches for Human Remains

The nature of police work is such that sometimes only vague clues are available regarding the location of a clandestine grave (e.g., “in farmer Brown’s bottom field.”). However, oftentimes without information of this type even the best available forensic tools have little hope of finding a grave. A variety of forensic tools can be used to locate clandestine graves. These are more efficient once the general location of a suspected gravesite is identified. The forensic methods range from non-invasive techniques to extremely invasive techniques, and include aerial photographic surveys of suspected areas, ground level photographic surveys, magnetometer and metal detectors, dogs trained to search for cadavers, ground penetrating radar, infrared photography, vegetation differential (pioneer plants), and penetrometer. Treatments such as wetting the site and then using ground penetrating radar and/or magnetometer, plowing the site and looking for color differential or other evidence of disturbances, and finally perform the actual forensic exhumation are also performed [1]. The overall objective of this project was to evaluate the feasibility of using chemical analysis to facilitate locating buried human remains and to ultimately develop a field portable chemical analyzer for this purpose. As described herein, chemical sensors can indeed detect the identified signature compounds. A proposed instrument design has been developed and is presented in Section IV.

#### I.1.1 Chemical Signatures of Decaying Humans

Our work builds on the work by Dr. Arpad A. Vass et al. [2] who demonstrated that specific chemicals are produced during decomposition of human remains. In this work unembalmed bodies were buried and surrounded by a series of sample collection tubes. For a period of one and a half years the chemicals exuded by the corpses were collected and analyzed. Eight major classes of chemicals containing 424 specific volatile compounds were identified. These chemicals represent chemical “signatures” for decomposing human remains and thus can be used to locate buried bodies. Three chemicals from the database were particularly interesting, Freon 11, 12 and 114 (trichloromonofluoromethane, dichlorodifluoromethane, and dichlorotetrafluoroethane) since they do not occur naturally in the environment and thus only occur because of some human interaction. They are exuded from human remains because they are formed as a result of ingestion of fluorinated water, which is especially prevalent in urban environments. In the work performed herein, our goal was to develop a field portable analyzer to detect the presence of chemicals that had been identified as markers for human decomposition.

#### I.1.2 Sensors and Instrumentation

The primary focus of the Phase I research plan was to identify the sensors that exhibited the best sensitivity to the signature chemicals associated with decomposing human remains. These sensors would serve as the detector for the proposed field-deployable instrument. Sensor evaluation was accomplished by exposing an array of chemical sensors to the signature chemicals. The resulting complex sensor response pattern was then analyzed to identify which of the sensors in this array gave the best distinct signals.

While working on electronic nose technology, Gopel and coworkers realized an array comprised of different types of chemical sensors was useful for detecting different classes of

chemicals [3-6]. In fact a hybrid array (e.g., one that is comprised of different types of chemical sensors) would outperform a comparably sized array assembled from a single type of sensor. Prior to this work, all sensor arrays were comprised of one type of sensor. As a result of the work by Gopel's group the MODular Sensor System (MOSES) electronic nose was developed. This is now a commercial instrument sold and serviced by Lennartz electronics. The sensor array within the IIT Moses E-nose is comprised of 4 electrochemical (EC), 8 Metal Oxide (MOX), and 8 Quartz Crystal Microbalance (QCM) sensors. For many applications, the hybrid array is often more successful than conventional arrays; in our case it allowed efficient screening of multiple sensor types for sensitivity to specific chemicals. The concept of "orthogonality" is central to the MOSES and the design of hybrid arrays. Orthogonal literally means at right angles'. In the electronic nose, orthogonality refers to the need for each sensor within the array to produce signals that are as different from each other as possible. With each sensor as a vectored dimension the goal of discriminating the signals from one chemical versus another chemical is more readily achieved if the signals happen in different directions [7]. Different sensor platforms (e.g., MOX, EC, QMB) are sensitive to different properties of the analyte. Thus, each element in a hybrid sensor array (comprised of different sensor platforms) would provide more unique information than individual elements in a classic array comprised of minor variations (e.g., coating types or additives) of one type of sensor.

Sensor response data is evaluated using various pattern recognition algorithms, including Principle Component Analysis (PCA). PCA is a means to transform multidimensional data (each sensor is a dimension) into two-dimensional space. This is accomplished with matrix manipulation of the output signals from the sensors. The visual representation of this will be a PCA plot with a nonlinear mapping routine that transforms a set of points from n (maximum 20) dimensional space to two dimensional space by maintaining the similarities and dissimilarities between the points, by minimizing the error function:

$$E = \sum_{i>j} 1/d_{ij} * \sum_{i<j} (d_{ij}^* - d_{ij})^2 / d_{ij}^*$$

where  $d_{ij}$  is the distance in n space and  $d_{ij}^*$  is the distance in two-dimensional space between the points i and j [8]. This gives rise to the PCA scores plot. Typically, data are presented as "score plots" which represent 90% confidence levels. The score plots are shown on two-dimensional plots as ovals around the data points. The Score Plot is a visual display of the data. Evaluation of the experimental data is based on the uniqueness of each chemical species within the PCA score plots. Chemical identification, although not impossible is more challenging with overlapping score plots. Overlapping score plots occur when the sensors array is not able to provide a unique response between targeted chemicals. Alternatively, well-defined and separated score plots represent unique response patterns in which the sensor signals can be used to provide specific chemical identification and with a higher degree of statistical confidence. When performing PCA, multiple identical tests are performed. The sensor data is normalized and averaged. When evaluating PCA score plots, we look for clear definition between plots associated with all chemicals in the data set.

The protocol to optimize sensor array design for the signature compounds of interest consisted of the following steps:

1. Develop the PCA score plots to show those chemicals that can be separated from the majority of other chemicals, which shows that unique patterns exist in the sensor array response that correspond to individual chemicals.
2. Identify and assemble a subset of sensors that respond distinctly to the target chemicals as indicated by unique PCA score plots. Data from the remaining sensors are disregarded since these devices do not contribute unique information. Excess or redundant sensors will add noise to a measurement and thus degrade analytic performance.

Accordingly, we tested target vapors using the 20 sensors present in the MOSES electronic nose as a screening system for determining the proper sensors to choose for the field instrument. A simple array system comprised of three sensors was shown to have optimal sensitivity to the signature compounds.

The ultimate goal of this project is to develop a field portable instrument designed to detect the chemical signatures associated with human remains. The chemical sensors are to serve as the detector element within the instrument. Such an instrument would complement the wide range of methods (dogs, ground penetrating radar, etc) already available to the forensic community [1]. It would add an important tool to better pinpoint remains during forensic exhumations. As discussed below the instrument could perform surface sweeps of the area, subsurface analysis of discrete locations, and analysis of soil samples. The ability of rapidly analyzing soil samples for target compounds could be especially useful during exhumations. In a forensic exhumation the suspected area is set into grids of one square foot. These grids are individually excavated ¼ inch at a time and the soil screened for evidence. Nothing may be pushed down into the soil due to concerns of contaminating or destroying evidence (e.g. a probe pushed through a skull can look just like a bullet hole). Our instrument will be able to examine the sifted dirt for target chemicals given off by decaying corpses. Such an approach could guide the exhumation by directing activity towards the area with higher signature compound concentrations.

We envision that the instrument would be cane shaped for ease of transport and manual insertion into soil. Operation would be by a rechargeable battery pack. User interface would be a conventional personal digital assistant (PDA, such as "Palm Pilot"). In addition to subsurface sampling a surface sweep mode will be available for rapid screening. Figure 1 shows a conceptual design for the field instrument. Further discussions are in Section IV. The instrument is to be developed in Phase II of this work.

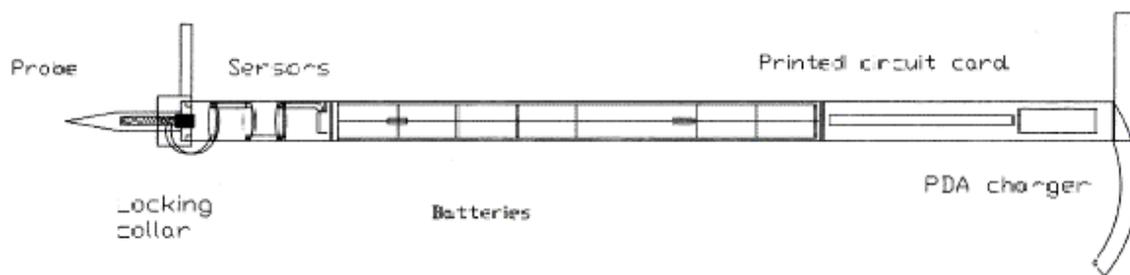


Figure 1. Proposed design for the chemical analyzer for performing on-site analyses of chemical signatures associated with clandestine graves. Details in text.

## II: Materials and Methods

### II.1 Chemicals

Proposed chemical signatures were identified from a review of the literature [2]. All compounds were obtained as pure chemicals, except for the Freons, which were obtained in a methanol matrix at 1000 ppm concentrations. Fuller's earth, used as a soil simulant, was purchased from Fisher. Appendix 1 lists all chemicals used in this study. In addition, Psuedo Scent, chemical mixtures that had been developed to train cadaver dogs, was purchased from Aldrich. All other chemicals were purchased from Fisher Scientific.

### II.2. MOSES Electronic Nose

Sensor evaluations were performed using the MOSES Electronic Nose (Lennartz, Germany) which is comprised of 8 MOX sensors, 8 QMB sensors, and 4 EC sensors. The MOSES is shown in Figure 2. Gas sampling and flow rates were controlled by an external pump and rotometer. Principle component analysis was performed using vendor-supplied software. PCA could be applied to all data and using all sensors. Alternatively, PCA could be performed on a user-selected subset of sensors. The sensor data was normalized and averaged prior to PCA.

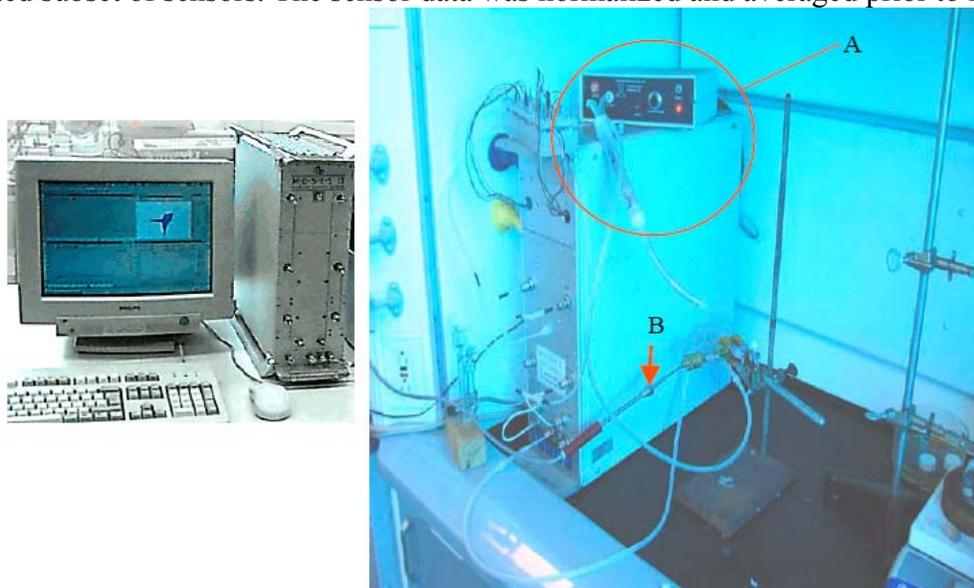


Figure 2. (Left) The Moses bench-top electronic nose, consists of up to 3 sensor modules and a computer system for data analyses. (Right) The test apparatus for Forensic Remains locator chemical testing. The pump (A) with purifying cartridge to provide clean uncontaminated air to pass over the pyrolyzer (B). Gas travels from the test chamber to the MOSES sensor modules, first to QCM module then it is split between the Electrochemical (EC) and the Metal Oxide sensors (MOX) module

Care was taken in the order in which the vapor samples were exposed to the sensors. While the QCM sensors may absorb a small amount of the sample, no transformation of the analyte occurs. Chemical reactions are however, associated with the EC and MOX sensors and this result in a change in composition in the gas stream. This is especially true for the MOX module since MOX sensors are heated catalytic beads that can change the chemicals in a gas stream. EC sensors are catalytic fuel cell like structures that will only slightly change the composition of the gas, but there will be some change. In order to avoid problems associated

with gas composition change and to observe the sensor response to the unaltered target chemical, we first passed the gas stream over the QCM and then split between the EC and MOX sensors.

### II.3 Test chamber and Sample Preparation

Soil simulants were prepared by mixing measured volumes of the target chemical with Fuller's earth to a final concentration of either 40 ppm<sub>w</sub>t (low) and 4% (high). The resulting mixture was placed inside a test chamber, which was filled to approximately ½ volume with the Fuller's earth/chemical mixture. The test chamber was custom-built from a ½" diameter brass tube. An end cap sealed one end of the chamber while the other end was fitted with a reducing union to narrow the diameter to ¼" so as to accommodate a commercial pyrolyzer probe (Pyroprobe, CDS Analytical company [9]). The pyrolyzer probe heated the soil/sample mixture. The pyroprobe was operated at two temperatures, high (300°C) and low (no added heat). Inlet ports (1/8" diameter) were fitted at each end of the main body of the test chamber to provide a pneumatic interface for vapor sampling. Flexible tubing was fitted over the inlet ports and interfaced the test chamber to the MOSES E-nose. Prior to passing through the test chamber, air was passed through a chemical filter (molecular sieves and Purafil™) which removed impurities present in the air. All external gas lines were Bev-a-Line™ (Cole-Parmer).



Figure 3 The test chamber. The pyroprobe was installed through the open end of the test chamber. Chemical mixtures in Fuller's earth would be preloaded into the test chamber prior to experimentation. .

### II.4 Test Protocol

The typical experimental test protocol was performed over 4 minutes and consisted of an initial baseline of about 10 seconds followed by introduction of the sample. Sensor background signals were made using filtered air that bypassed the test chamber. Background air and sample flow to the sensors were controlled by a manually operated 3-way valve. The gas flow rate was set at 40 ml/min as controlled by a rotometer mounted on the exhaust of the MOSES. Tests were performed with the pyroprobe at room temperature and with the pyroprobe heated to 300°C. Typically, three replicates of each condition (sample type, temperature) were performed.

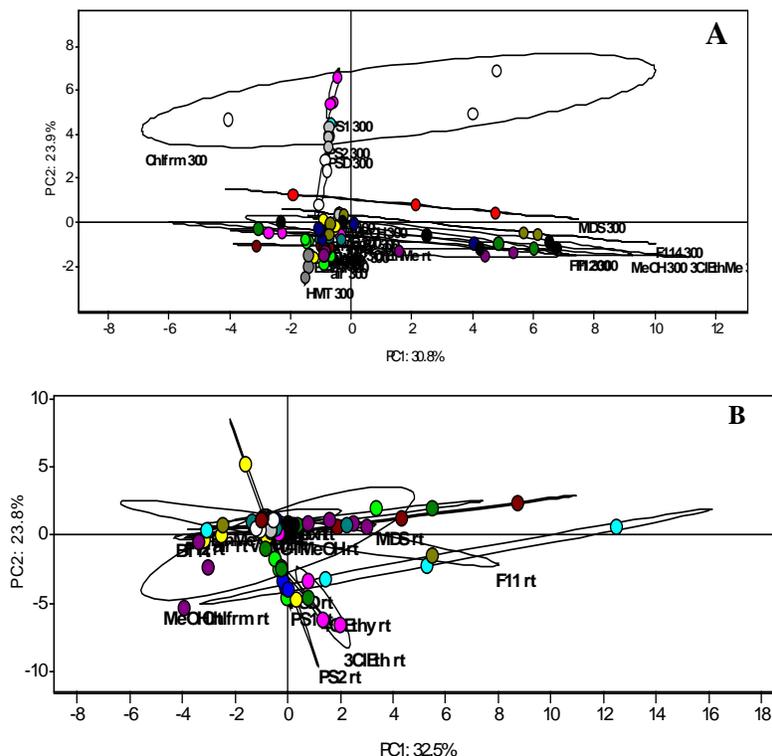
### III Results

Tests were performed in two distinct groups of high or low concentrations of the target chemicals. The high concentration test was performed first. This allowed development and assessment of the experimental protocol and data analysis methods. High temperature (300°C) and low temperature (no activation of the PyroProbe) tests were performed for each concentration of the target chemical (4% and 40 ppm<sub>w</sub>t).

#### III.1 High Concentration Testing

Vapors were exposed to the Moses E-nose and evaluated using the supplied software for Principle Component Analysis (PCA). Resulting score plots (all chemicals and all sensors) are shown in Figure 4. Figure 4A is for data collected with the Pyroprobe at 300°C, while 4B is for room temperature conditions.

As discussed in the introduction, large sensor arrays do not necessarily outperform a smaller array, especially if the smaller array was engineered for the specific application. Figure 4 shows score plots generated using responses from all 20 sensors within the Moses sensor array. Within the array, there are 8 MOX sensors. Each MOX sensor was selected because of specific analytical performance, but these sensors are not totally unique to the chemicals of interest for decaying bodies and therefore the information content between sensors can be redundant. The presence of a large number of redundant or near-redundant sensors can actually add noise to the data and degrade performance in PCA analysis.



Figures 4 PCA scores plots obtained with all sensors and all chemicals. A: PCA of data with the Pyroprobe at 300°C. B: PCA plots for data obtained with the Pyroprobe at room temperature. As can be seen there is very little separation of the scores from each other. Only Chloroform and the pseudoscent mixtures stand out at 300°C.

One strategy to circumvent problems with a large array is to use a sensor array with a minimal number of sensors, each of which should be selected because of its sensitivity to the vapors of interest [7]. This strategy was invoked herein where we investigated a subset of the MOSES array. The modified array consisted of electrochemical (EC) sensors 1, 2 and 4. EC 1 has a gold working electrode and operates at a bias of  $-100$  mV, EC 2 is also gold but with a  $+300$  mV bias, EC 4 is a platinum working electrode with a filter and  $+150$  mV bias. This combination was selected based in part by intuitive understanding of sensor sensitivity to the desired chemical and by trial and error, observing the effect on the score plots with each change in the array. Scores plots generated using data from this 3-sensor array are shown in Figure 5. Several chemicals separate from the bulk of other chemicals, indicating that these sensors can distinguish these chemicals. The score plot separations are shown in Figures 5 to 15. In the following group of figures one chemical or small group of chemicals is identified, that is it shows up as separated from the others in PCA space (see figure 5). That chemical or group is removed from the training data set and PCA is performed on the remaining data (see Figure 6). A new score plot is formed, and we found that a new group or chemical can be identified as indicated by a well-separated score. This chemical is then removed from the data set and PCA repeated again. The procedure was repeated until no distinction was noted between the remaining chemicals in the data set background air (see figure 15). Successive removal chemicals with separated plots gave the following list of distinguishable chemicals: (step 1) Methanol, (step 2) all PsuedoScent® mixtures, Hexamethenetramine at  $300^{\circ}\text{C}$  (HMT 300), Benzenedimethanol at  $300^{\circ}\text{C}$  (BZDM 300), Tetrachloroethylene at  $300^{\circ}\text{C}$  and room temperature (4ClEthy 300 and RT), (step 3) MDS  $300^{\circ}\text{C}$  & RT, (step 4) Chloroform  $300^{\circ}\text{C}$  & RT (Chfm 300 & RT), (step 5) Freon 11  $300^{\circ}\text{C}$  and RT, (step 6) Freon 12 RT, Freon 114  $300^{\circ}\text{C}$  & RT, (step 7) Benzthiozole (BT RT), Trichloroethylene (3ClEthy  $300^{\circ}\text{C}$  and RT), (step 8) Undecane (UN RT), (step 9) Valeric Acid (VA  $300^{\circ}\text{C}$  and RT), (step 10) Butyric Acid (BA  $300^{\circ}\text{C}$  and RT), Heptane (Hept  $300^{\circ}\text{C}$  and RT), BT  $300^{\circ}\text{C}$ .

Separation of the score plots affirm that the sensors response is significantly different for these chemicals. This is promising for detecting clandestine graves. We have identified several signature chemicals that can be distinguished from each other and from the bulk of other chemicals using only three sensors. This can form the basis of a hand held instrument, with the caveat that the concentration was rather high at about 4%. Performance at lower, more realistic concentrations is described in the next section.

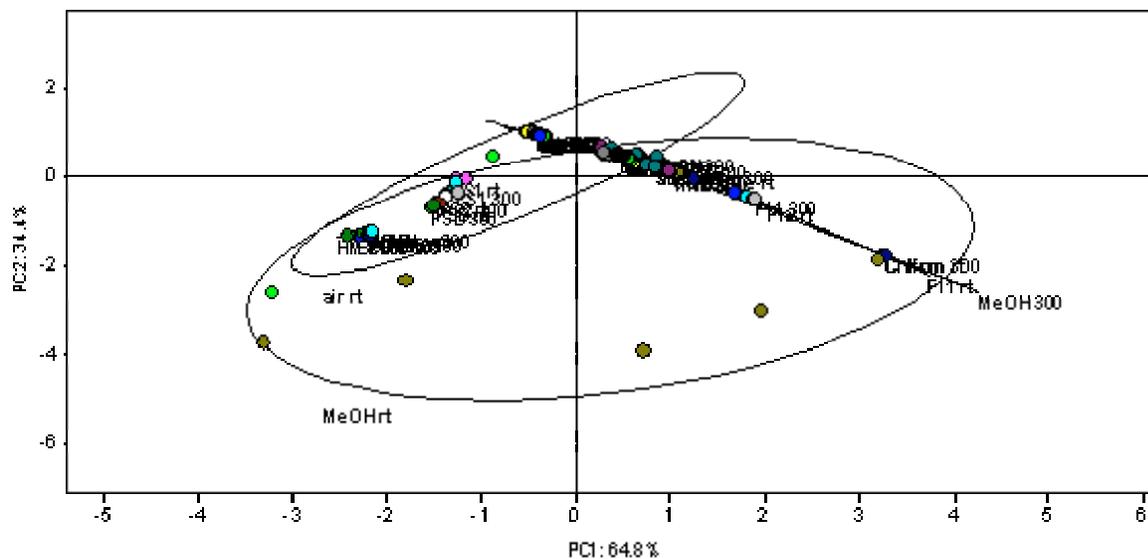


Figure 5. PCA score plots obtained with normalized, average data from EC 1,2 and 4. All chemicals used. Note methanol (●) gives distinct score plots, the rest of the chemicals are aggregated near the origin indistinguishable from each other. Procedures to separate the score plots of this aggregate are discussed in the text.

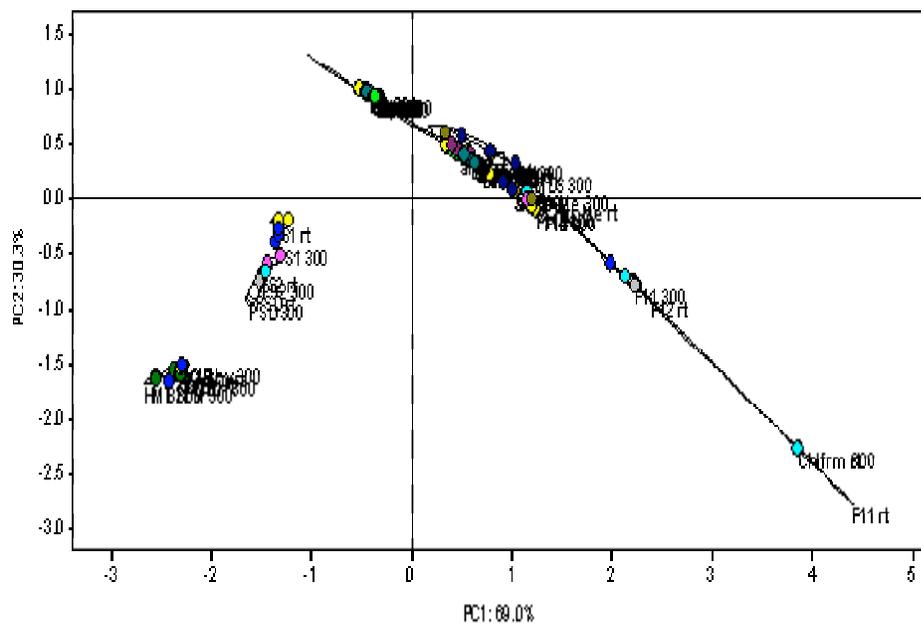


Figure 6. Same as figure 5 but with Methanol removed. The group over on the lower left is comprised of HMT 300 (●), 4CI 300 and rt (●), BZDM 300. The upper group above is the Pseudo Scent compounds rt and 300 °C (●, ●, ●, ●).



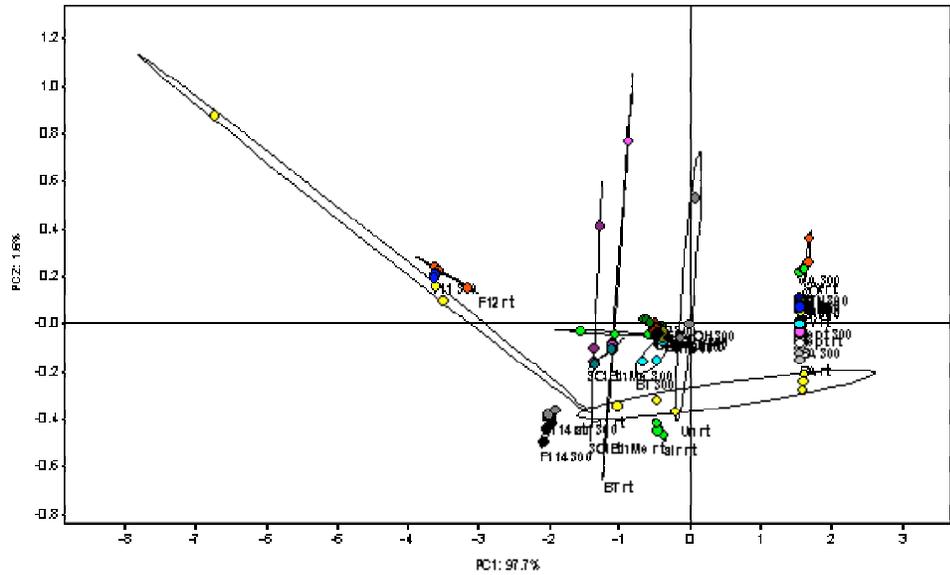


Figure 9. Same as figure 8 but with Chloroform removed. Upper left is Freon 11 rt and 300°C (●●).

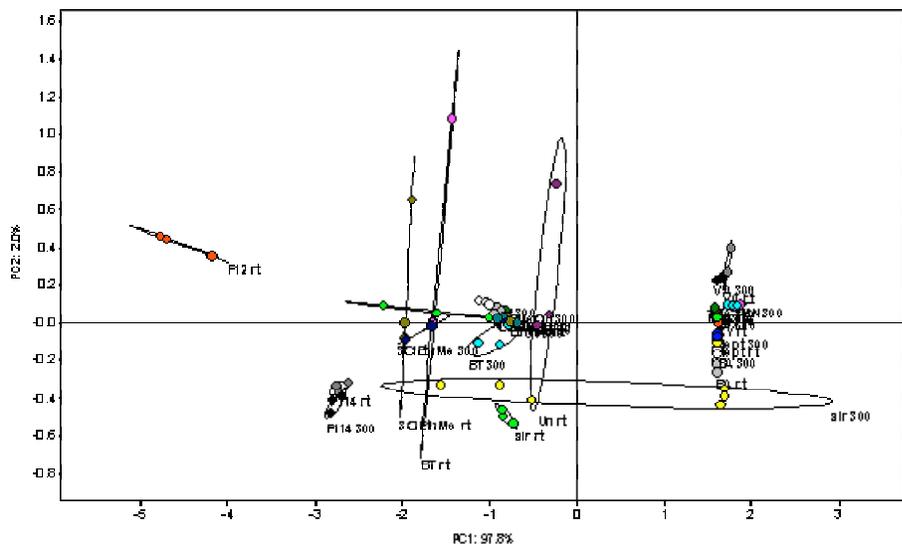


Figure 10. Same as figure 9 but with Freon 11 removed. Upper left is Freon 12 rt (●), below and to the right is Freon 114 rt and 300°C (●●).

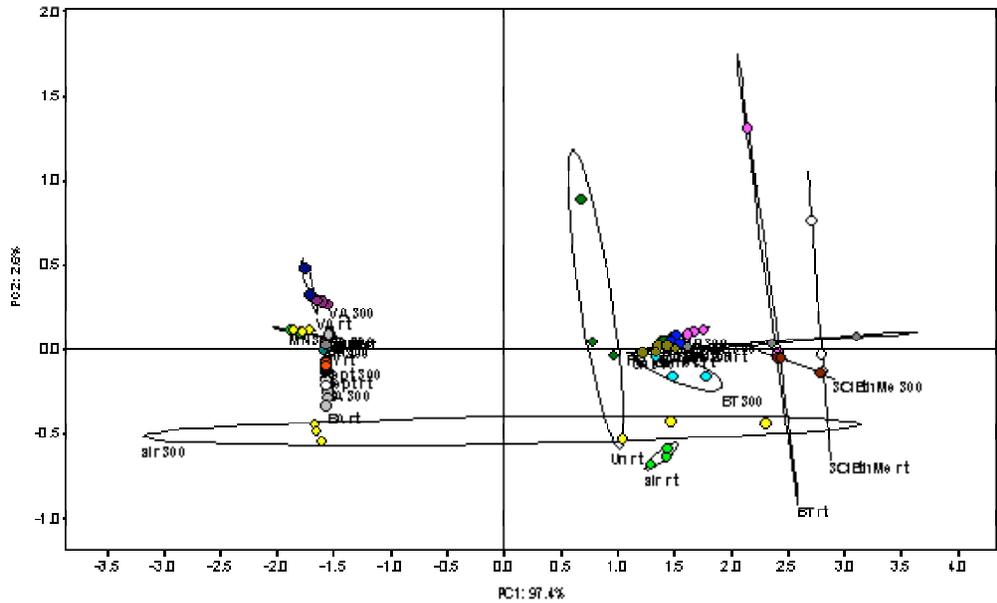


Figure 11. Same as figure 10 but with Freon 12 and 114 removed. Far right is 3CIETHy rt and 300°C (●●), also BT rt (●).

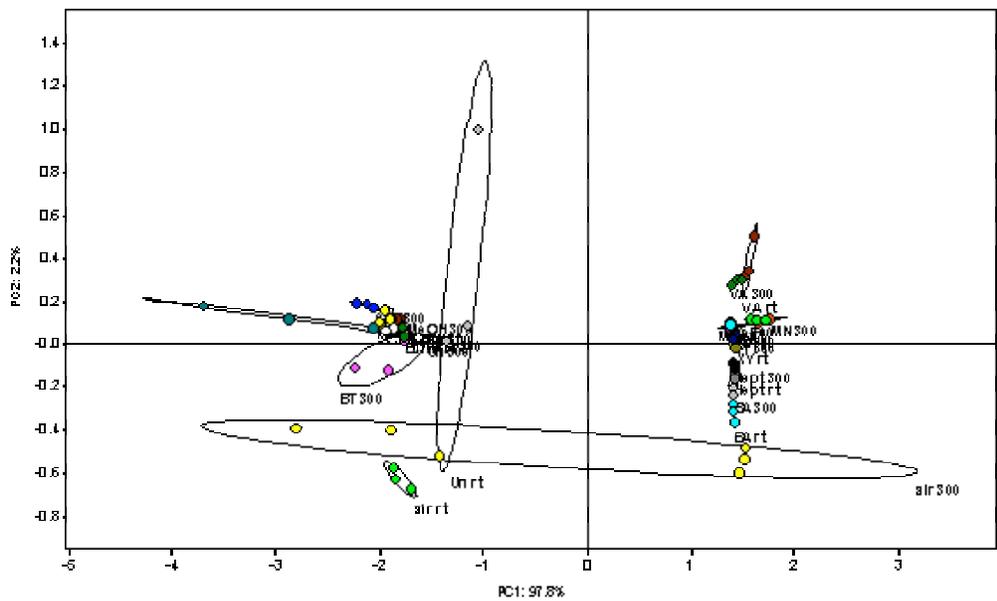


Figure 12. Same as figure 11 but with 3CIETHy and Bt removed. Un (●) clear at center top.

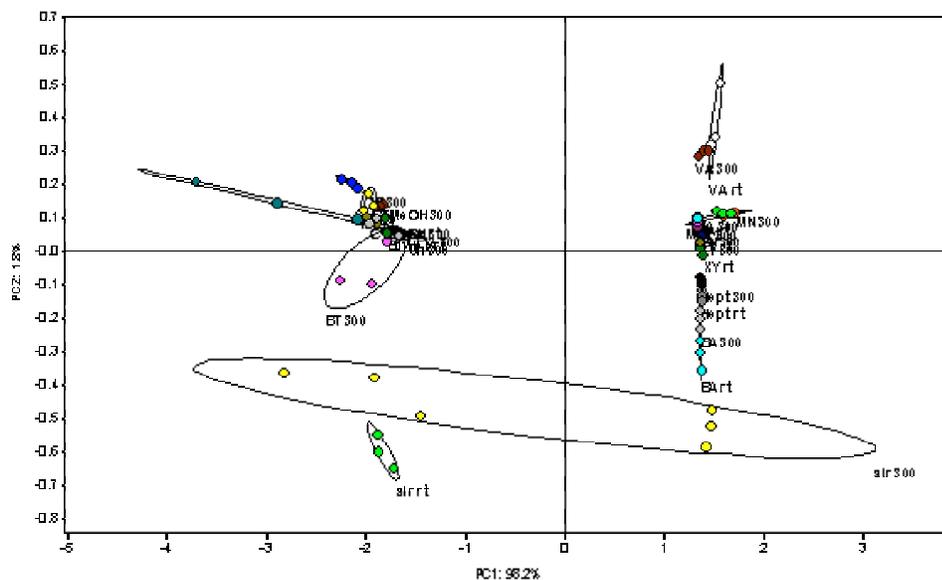


Figure 13. Same as figure 12 but with 3ClEth and Bt removed. VA (●●) right top distinct from rest of chemicals.

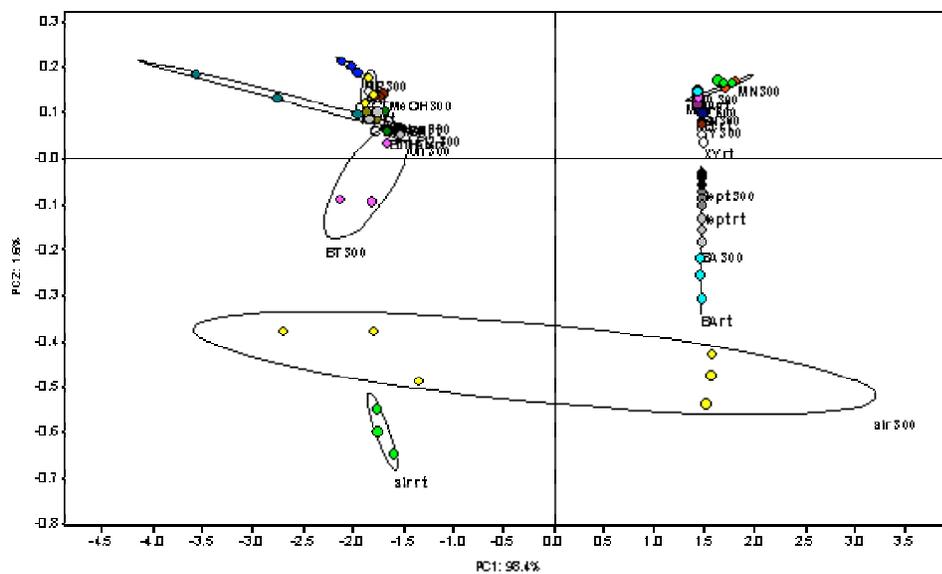


Figure 14. Same as figure 13 but with VA removed. Mid left BT 300, Mid right group Hept rt and 300°C (●●), BA rt and 300°C (●●) are clearly separate in the PCA matrix from the rest of the chemicals.

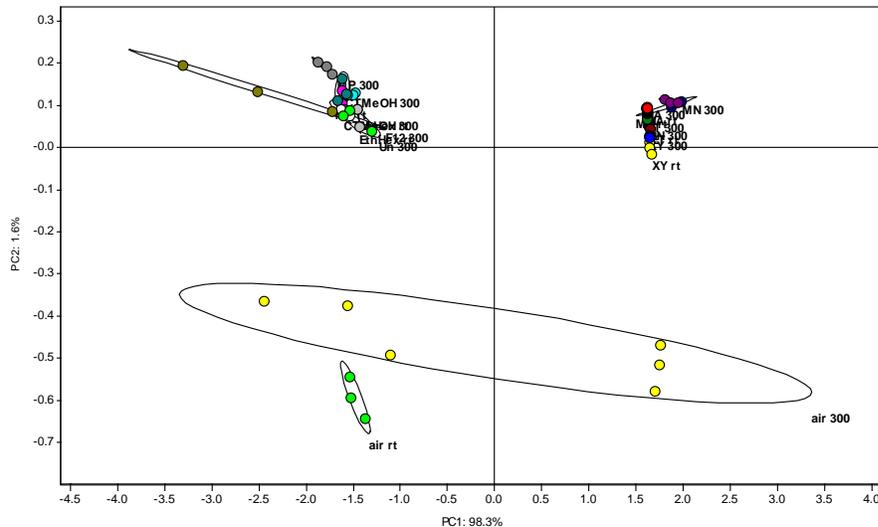


Figure 15. Same as figure 14 but with BT, Hept, and BA moved. None of the groups stand out; air background (●●) is most prominent thus none of the other chemicals would be distinguishable from the background air.

### III.2 Low Concentration

The above evaluations were performed on sensor data collected with high chemical concentrations. Using the high concentrations, a procedure was developed that provided encouragement that the electronic nose can be tuned for signature compounds of interest. Tests were then performed at a significantly lower chemical concentration of 40 ppm to determine if the approach would work at more realistic concentration. Three test exposures were performed at each temperature (room temperature and 300°C) on each of two days to provide six data sets for each condition.

Data sets were combined and evaluated with the MOSES PCA software. Signals generated from the freons and methanol were very strong. It should be noted that Freon samples were commercially obtained as solutions of 1000 µg/ml in methanol. 100 µl of this was used on the 2.5 grams of Fullers Earth to give 40 ppm. The methanol matrix may be a main cause of a large Freon response, although the score obtained for Freon is different than that of methanol. Figures 16 and 17 show principal component analysis (PCA) plots of all sensors. Figure 17 presents score plots obtained with the freons and methanol runs removed from the data set.

Through trial and error, EC sensors 1,2 and 4 were found to provide the optimal unique response profiles as indicated by the PCA plots. Separation of many chemicals was achieved before the background signal dominated the response patterns. The specific chemicals detected in this way were: Freons and Methanol (possible problems discussed above), Methylsulfide (MDS), Undecane (UN), Xylene (XY), Benzthiozole (BT), Methylnaphthalene (MN), Tetrachloroethylene (TetClEth). The separated score plots indicates that the use of these 3 sensors give clear definable analytical information that will allow identification of these signature chemicals. No other grouping of sensors and parameters was identified that would give close to this number of distinguishable chemicals.

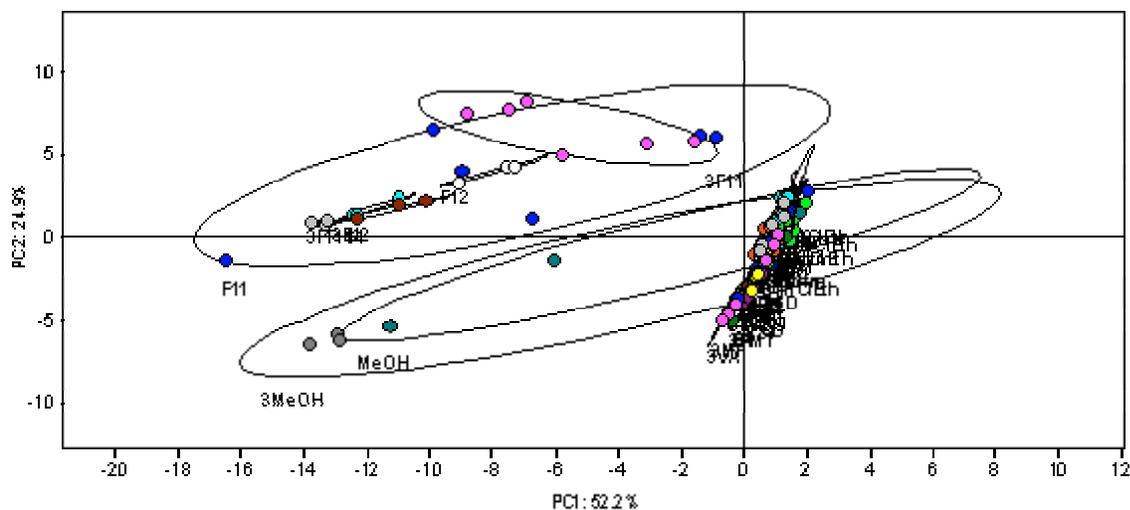


Figure 16. 3-component PCA plot (two shown) performed using, standardized averaged data. All sensors and chemicals were used in the PCA. Freons (●●●●) and methanol (●●) are clearly separated showing that they can be distinguished from the other chemicals.

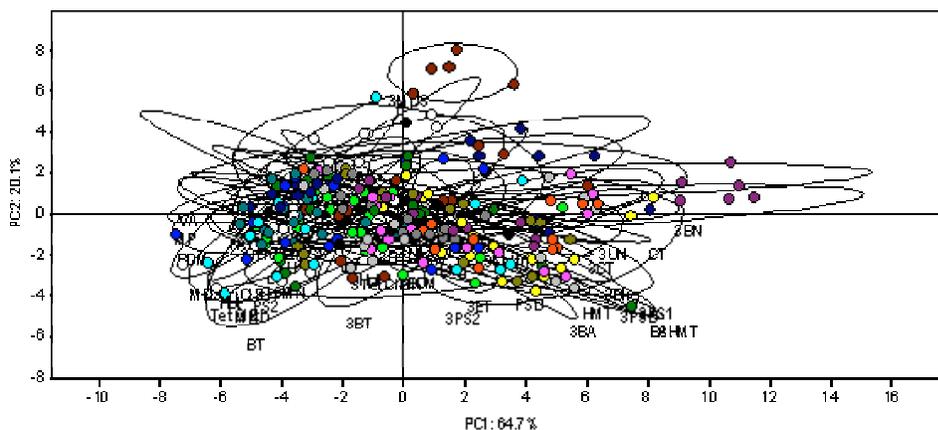


Figure 17. PCA perform in a manner identical to that described in Figure 1 but without the freons and methanol data. In this score plot, Methyl disulfide (MDS, ●) shows score plot separation, but all other chemicals are group into overlapping score plots. When MDS is removed there is no separation.

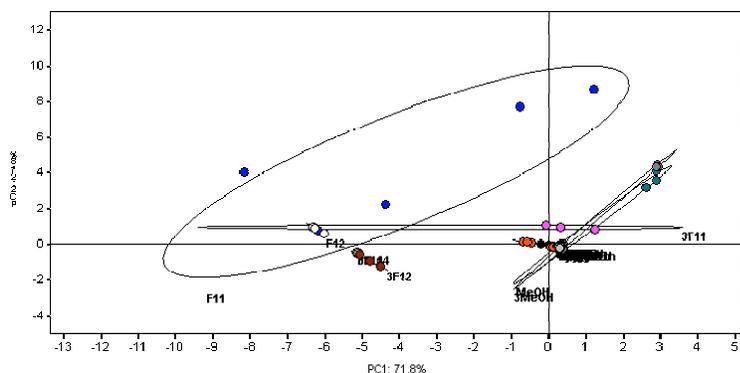


Figure 18. Low concentration (40 ppm). 3 component PCA with normalized, average data using EC 1,2 and 4. All chemicals used. Note Freons (●●●●) and methanol (●●) give distinct score plots, the rest of the chemicals are aggregated near the origin indistinguishable from each other. Procedures to separate the score plots of this aggregate are discussed in the text.

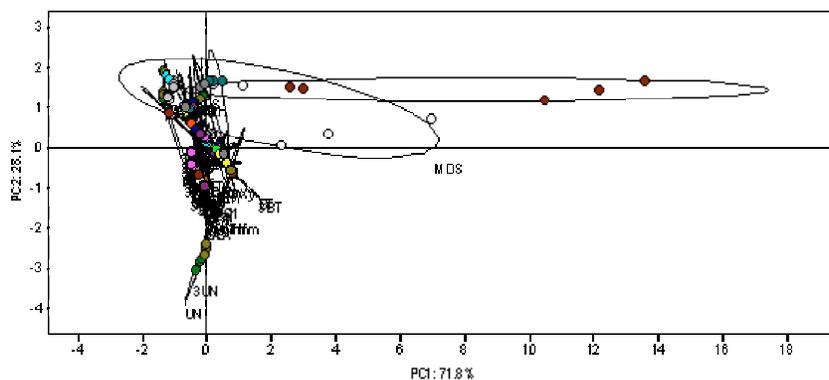


Figure 19. Identical to figure 18 except Freons and Methanol removed from the data set. PCA performed on the remaining chemicals. The resulting score plots show distinct separation for MDS (●) at room temperature and 300°C. With many of the sensor groups evaluated but not reported MDS often had clear distinction from other chemicals in the PCA space.

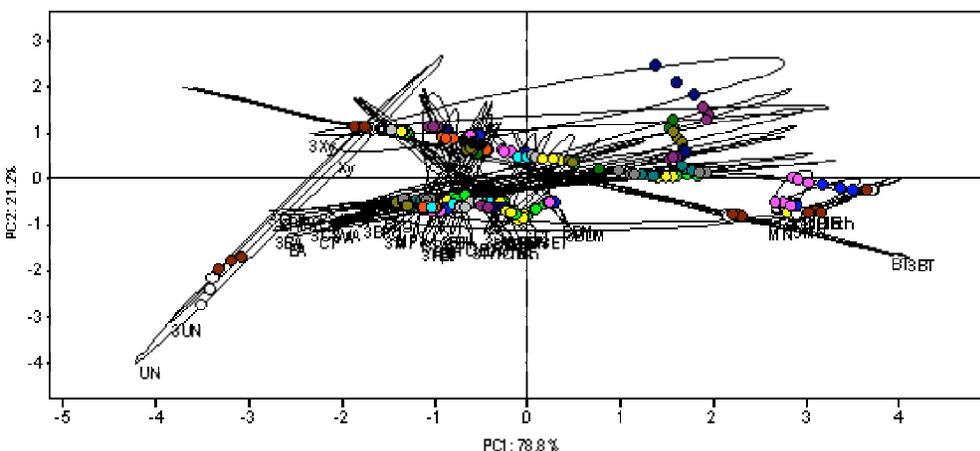


Figure 20. Identical to figure 19 except MDS removed. This allows score plots associated with other chemicals to be separated: UN to the left (●), XY above (●●), and BT to the lower right (●), temperatures overlap. In an instrument for detecting human remains it is hoped that the signals from the sensors created by these chemicals would be clearly separate from the background.

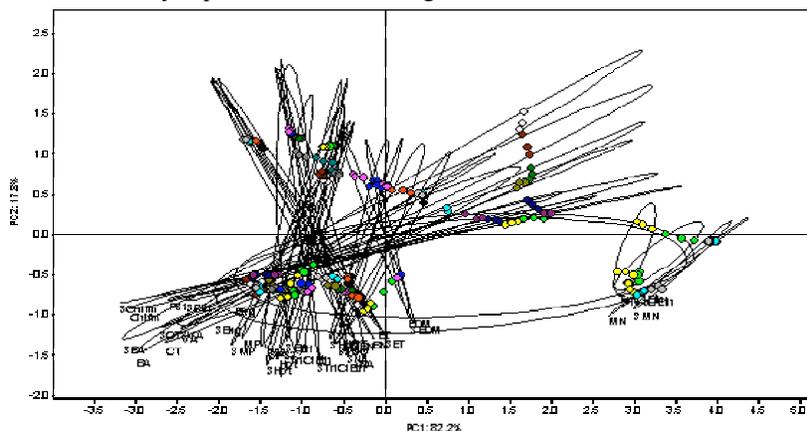


Figure 21. Same as figure 20 but without UN, XY and BT in the data set. MN (●●) and TetClEtH (●●) to the right separate from the other chemicals.

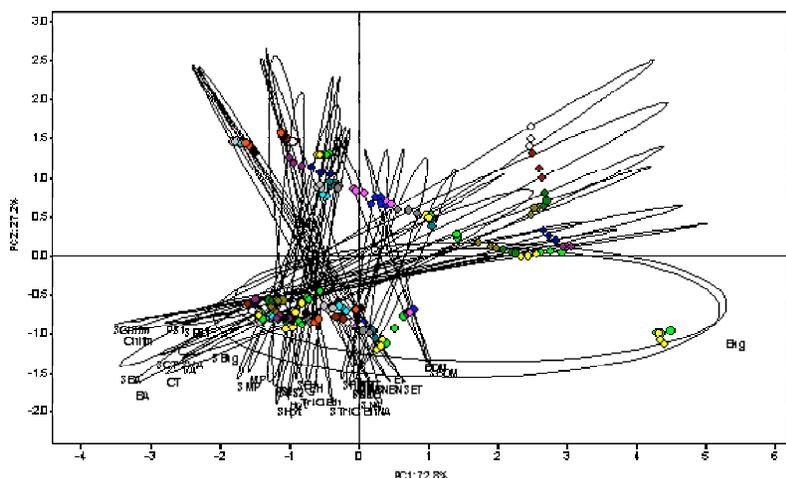


Figure 22. Same as figure 21 but with MN and TetClEth removed from the data set. The score for background air (●●) is most dominant and distinct score require simple electronic circuitry, and they have good stability of signal (generally lasting a half year).

This method of analysis (PCA with standardization on the average signal) led to the expectation that with appropriate software these three sensors could identify low concentrations of six critical signature compounds at low concentrations (excluding freons and methanol). These six compounds are spread across five different classes (two sulfur compounds, non-cyclic hydrocarbons, cyclic hydrocarbons, halogen, and lipid derived). This is a wide range of classes. From the way these classes differentiated, heating the soil will not change the electrical signal from the sensor but is expected to volatize significant quantities of these chemicals from the soil matrix. The data from a three-sensor array is sufficient to perform these analyses.

### III.3 Sensor Selection

Using three electrochemical sensors simplifies the instrument design. Electrochemical sensors use very little power and they have good stability of signal (generally lasting a half year). Commercial devices exist that can readily fit within the probe (Section IV). Furthermore, electrochemical sensors require simple control circuitry and there exist standard designs (Figure 23).

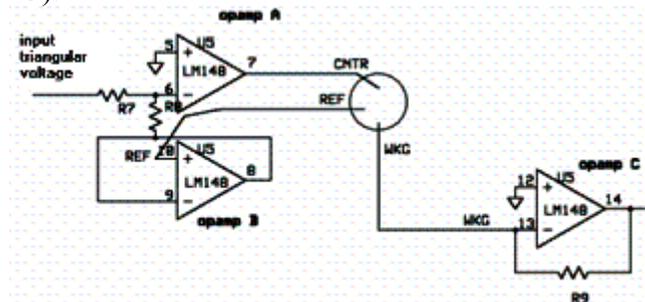


Figure 23. A typical electrochemical circuit [10] consisting of three operational amplifiers (a small integrated circuit) and three resistors.

At the International Center for Sensor Science and Engineering at Illinois Institute of Technology several potentiostat instrument systems have been developed. One of these was a miniature round circuit card for detecting leaks on chlorine tank cars for the railroad industry. Miniaturization of the control circuitry is very useful as it allows ready deployment within the

proposed tubular design of the instrument (see Figure 1). Figure 24 shows the sensor along with the miniature potentiostat board. The electrochemical sensors used in our evaluation were similar to commercial sensors currently manufactured by the Transducer Technology division of KWJ Engineering (Newark, CA).



Figure 24. Miniature potentiostat circuit card (approximately 3 cm in diameter) and EC sensor similar to the type recommended for detection of clandestine graves. The device is 1.25 inch in diameter. EC sensors with smaller geometric features (0.6 inch diameter) are also available.

## IV: Instrument Design and Development

### IV.1 General instrument

As envisioned at the onset of this project, the proposed design would be a cane-shaped instrument that can be pushed into the soil and other modes of operation. A concept is illustrated in Figure 1. Figures 25 to 29, discussed below, focus on additional design features of the proposed instrument.

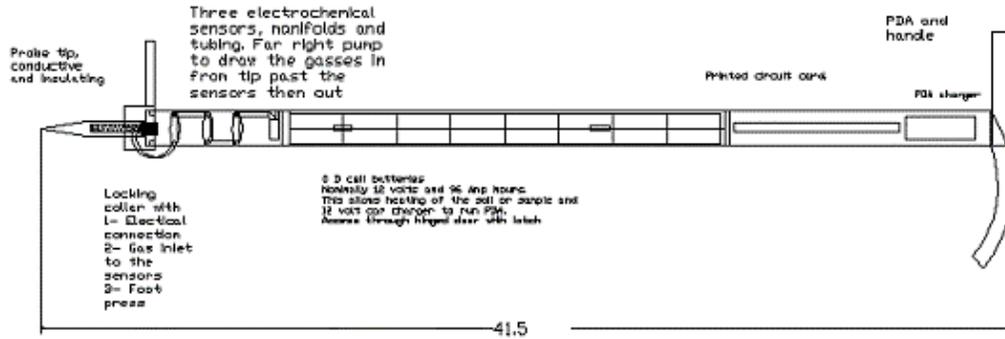


Figure 25. Detailed view of proposed forensic remains locator. Generally this is a tube 1 3/4" diameter and approximately 41 1/2" long. Different components are described in Figures 26 to 29.

The top end of the cane type instrument is straightforward. Instrument control will be performed by a laptop computer or a personal digital assistant (PDA) computer. The computer will perform all the data acquisition, evaluation, and user interface and can be mounted on the handle of the instrument (Figure 26). The PDA battery can be charged using readily available automobile type charger units to facilitate field operations. The programming of the computer is certainly a complex task but not insurmountable and well within the capability of resources available to the ICSSE. The minicomputer would need to be programmed to allow automated operation, including presentation of results, by field personal with minimal training. The interface to the user would have to be developed for our forensic probe, but such algorithms have been developed in portable E-nose instruments [11].

Power for the sensors, pumps, and pyrolyzer will be provided by a battery pack mounted within the shaft of the probe. The shaft of the probe is of such size that it can accommodate D cell batteries or other batteries of equivalent dimensions (e.g., NiMH rechargeable batteries) as shown in Figure 27. A printed circuit card will handle power management for instrument operation as well as to provide connections between the various electrical subsystems.

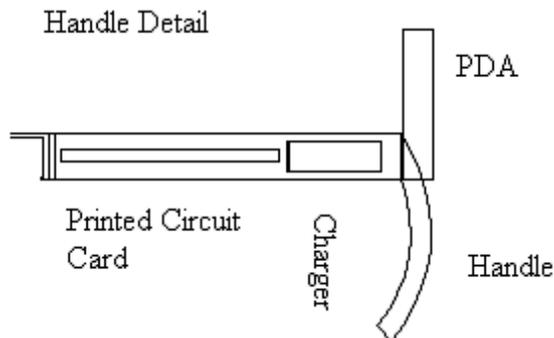


Figure 26. Upper handle area detail.



Figure 27. Battery compartment. The shaft can readily accommodate the battery pack.

## IV.2 Probe Tip

At the base of the instrument is the Probe Tip, which provides the interface between the external environment and sensors. A foot press is attached at the base to facilitate manual insertion into soils. The Probe Tip connection to the body of the “cane” will be a threaded  $\frac{1}{2}$ ” collar to hold it in place while the collar is placed on. The collar is where the force is applied vertically to the ceramic probe. The collar is also where the electrical and pneumatic connections are made to the probe. Just above the probe tip and internal to the instrument, the sensors and control circuitry will be mounted (Figure 28). The sensors are commercially available and the interface board designs are well characterized. A small pump will pull gas through the probe tip and past the sensors. The sensors will be located near the bottom of the instrument, close to the gas inlet to avoid condensation of the vapors and other undesirable processes that might occur with long transfer lines (Figure 29).

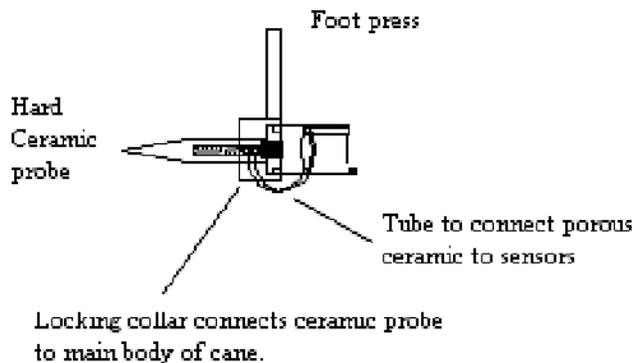


Figure 28. Probe and collar detail.

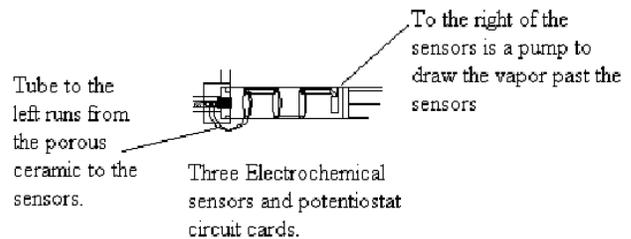


Figure 29. Sensor and pump detail.

The probe tip is a critical component of the instrument. It serves as the interface between the soil sample and the internal instrument system. The probe tip fulfills numerous functions including:

1. Pressed into the soil with considerable force (mechanical robustness)
2. Heat the surrounding soil to volatilize condensed chemicals
3. Allow transport of soil gases to the sensors
4. Filter incoming gasses to prevent particles from damaging the internal sensors and pumps
5. Provide a conduit for make-up gas to be flush back into the soil cavity to facilitate sample collection.

Numerous designs for the probe tip can be considered. Metal probes with heater elements have been used with the cone penetrometer, and these were successfully deployed to depths of 150 feet [12]. Hand operated soil gas probes and methods have been developed [13]. For the proposed instrument, a ceramic-based prototype design was developed, an approach that allowed rapid in-house prototyping. The main body was fabricated with a moldable, hard dense ceramic (e.g., Red Art). Figure 30 shows a prototype. The ceramic was formed into a tapered bit 0.7” in diameter and 5” long and sintered. The mechanical strength of the ceramic should be deployable in most soil types, and certainly for those applications where the probe is manually

pushed into the soil (see foot press in Figure 28). This of course will be demonstrated during field testing.

The probe tip must accommodate an external heater element and gas inlet system. One approach already investigated was to modify the probe tip by cutting channels along the length. Connecting these channels is a hole bored through the center. A porous, conductive clay can fill the channel and hole. The porosity and conductivity can be controlled by weight ratios of water and loading with graphite. A material with about 0.02 cc/min/square inch/psi of water flow and about 14 ohms resistance per centimeter distance was produced. The porosity of the ceramic allow vapors to be collected through the probe tip. Air flow of up to 60 cc/min was maintained through the porous ceramic material; this flow rate is compatible with the requirements of the electrochemical sensors. The conductive properties of the ceramic were evaluated as an integrated heater, but this proved to not be practical. Too much electrical power was required to heat. Instead an embedded heater/pyrolyzer is under consideration. Prior the setting a platinum heater wire can be embedded into the ceramic just below the hole. This design can easily operate at  $T > 300^{\circ}\text{C}$  under battery power, the thermal conditions deployed during Phase I sensor evaluation.



Figure 30. Probe tip during the shaving process (heater design and installation). The shiny part is graphite impregnated ceramic. The bolt on the top is used for forming a 1/2" thread.

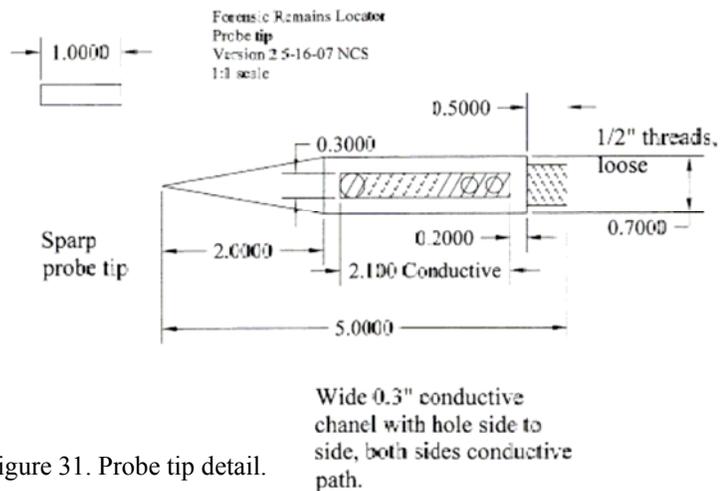


Figure 31. Probe tip detail.

### IV.3 Data Acquisition and Control

Data acquisition and control will be based on a commercial platform such as LabView™ (National Instruments). LabVIEW is recognized as a leading graphical programming platform.” [14] for data acquisition, experimental control, and data workup. LabVIEW PDA for PocketPC is available for use with Windows CE or PocketPC/ Windows Mobile operating systems. With over 600 MHz processing speed and 300 MB memory these PDA systems far exceed the 30 KHz and 256 KB systems in use with the first electronic nose in 1985 [15]. The NI CF-6004 with 4 channels of analog input and 4 digital input or output lines is a data acquisition and control system available from National Instruments that should meet the needs of this instrument. At just 16 cm<sup>2</sup> and fitting into a type II compact Flash slot, size is certainly not an issue and power consumption of 68 mA maximum falls well within the power budget.

#### IV.4 Operational Modes

The proposed forensic probe has three general mode of deployment, which include both in-situ and surface operation. In in-situ deployment the probe would be inserted into the soil, a process facilitated by the foot press, and a manually initiated analysis would be activated. Soil gas would be sampled and analyzed. Similarly, a surface sweep of the area could be performed. In this analyses could also be manually initiated, but in this case, the area just above ground level, as opposed to within the soil, would be analyzed. In both cases the PDA would provide an indication of the presence and amount of signature chemicals. Repeated analyses should serve as a guide to the likely location of buried remains.

The final mode of deployment would serve as a tool to support on-going forensic exhumation activity. Forensic exhumations is a time consuming task; soil can only be removed a quarter inch at a time from one foot square sections of the suspect site. This soil must also be sifted for evidence. Since forensic exhumations are slow, a means to guide the process could be extremely beneficial in terms of cost and time. In this mode a cup filled with soil can be used for analysis. The soil would be a grab sample obtained from the exhumation. The presence (or absence) of signature compounds can help guide the forensic search.

## Section V: Conclusions and Future Work

Detecting clandestine graves is fortunately a rare occurrence. Most of the effort is performed by police detectives and in identifying the approximate location. Numerous methods are available to locate the clandestine gravesite. The chemical analyzer would be another tool for this operation. Cadaver dogs obviously respond to chemical signatures. But an electronic instrument has some advantage over dogs. Due to the need to preserve evidence, excavation needs to be performed very slowly and carefully. In the excavation process it may be necessary to have the cadaver dog and handler on site for the many hours. Ultimately canine fatigue becomes problematic. There are also applications where a machine would be analytically superior to canines. Areas that may be laced with distractive odors can be problematic. For example, a dog handler at the class of NecroSearch International stated that human excrement smells just like decaying flesh to dog. This is a possible interferent that would result in a false positive. Thus, the use of chemical signatures at campgrounds and waste dumps can be problematic with dogs. An electronic analyzer can be tuned against such interferences. The proposed instrument will detect a different mix of chemicals that are specific to human decomposition. The fluorine compounds identified by Vass [2] are one such promising signature.

### V.1 Future Work

Significant work has been performed in identifying viable sensors types that would be effective for determining the location of clandestine human graves. This project was developed as a collaboration between the Illinois Institute of Technology (IIT) Center for Sensor Science and Engineering (Dr. William Buttner, Principal Investigator), Argonne National Labs (John Schneider), and Illinois State Police Forensic Science Center (Scott Rochowicz). The test and development stage of the project was performed and organized at IIT. At the end of Phase I we have determined the best sensors to use in a hand held instrument would be three electrochemical sensors. The proposed Phase II plan is to produce and test of prototype instruments with these sensors. Phase II will include field evaluations, and thus will have increased active collaborations from the other group members. John Schneider and resources available from Argonne will assure the accuracy of the instrument and provide laboratory verification of the measurements. The Forensic Science Center will review the instrument design and make recommendations. The Forensic Science Center will also identify possible sites for deployment studies and facilitate access to these sites. Initial design work has been performed on a prototype instrument. More work on the Instrument is still needed, as itemized below

- 1) Probe design development
  - a. Robust, operation In-Situ heater element (embedded wire)
  - b. Gas extraction from a soil matrix (pneumatic system)
  - c. Need for pushing make-up air into the soil to increase the flow of chemicals to the sensors (pneumatic system)
  - d. mechanical robustness to allow repeated use in real world environments
  - e. replaceable design to allow easy in-the-field repairs
  
- 2) Collar design including
  - a. Connection to the foot peddle
  - b. Electronic and power conduit
  - c. Pneumatic connections

- d. Method of ensuring all downward and sideways force to the probe goes through the collar
  - e. Mechanic interface of probe tip to instrument
- 3) Software design including
- a. Method to drop the highest recognized signal and find the next one
  - b. System to make it easy for the novice to use

## References

1. NecroSearch International class literature June 2006.
2. "Decompositional Odor Analysis Database" Arpad A. Vass, et. al., Journal of Forensic Science, July 2004, Vol 49, No. 4
3. Heiko Ulmer, Jan Mitrovics, Gerd Noetzel, Udo Weimar, Wolfgang Gopel "Odours and favours identified with hybrid modular sensor systems" Sensors and Actuators B 43 (1997) 24-33.
4. W. P. Carey, K. R. Beebe, B. R. Kowalski "Selection of adsorbates for chemical sensor arrays by pattern recognition", Anal. Chem. 58 (1986) 149-153.
5. D. S. Ballantine, S. L. Rose, J. W. Grate, H. Wohltjen, "Correlation of surface acoustic wave device coating responses with solubility properties and chemical structure using pattern recognition" Anal. Chem. 58 (1986) 3058-3066.
6. W. P. Carey, B. R. Kowalski "Chemical piezoelectric sensor and sensor array characterization", Anal. Chem. 58 (1986) 3077-3084.
7. M. Pardo, L.G. Kwongb, G. Sberveglieri, K. Brubaker, J. F. Schneider, W.R. Penrose, J.R. Stetter; "Data Analysis for a Hybrid Sensor Array," Sensors and Actuators B 106 (2005) 136-143.]
8. J. R. Stetter, P. C. Jurs, S. L. Rose, "Detection of hazardous gases and vapors: pattern recognition analysis of data from an electrochemical sensor array", Anal. Chem. 58 (1986) 860- 866.
9. <http://www.cdsanalytical.com/products/p5000.htm>
10. Ashwini Vittal Gopinath, Dale Russell, "An inexpensive field-portable programmable potentiostat", The Chemical Educator, Vol. 11, No. 1, Dec. 6, 2005
11. Young Rebecca C; Buttner William J; Linnell Bruce R; Ramesham Rajeshuni "Electronic nose for space program applications." Sensors and actuators. B, Chemical (2003), 93(1-3), 7-16.
12. William J. Buttner, Melvin Findlay, William Vickers, William M. Davis Ernesto R. Cespedes, Stafford Cooper, Jane W. Adams, "In-Situ Detection of Trinitrotoluene and Other Nitrated Explosives in Soils" Analytica Chimica Acta, 341 (1997) 63-71.
13. Soil Gas Sampling, EPA SOP # 2042, (June 1, 1996)  
<http://www.dem.ri.gov/pubs/sops/wmsr2042.pdf>
14. [http://www.ni.com/labview/presskit\\_awards.htm](http://www.ni.com/labview/presskit_awards.htm)
15. Stetter, Joseph R.; Penrose, William R.; Zaromb, Solomon; Nolan, Matt; Christian, Donald; Hampton, Diana; Billings, Michael; Steinke, Carl; Stull, Jeffrey O. "A portable toxic vapor detector and analyzer using an electrochemical sensor array". Analysis Instrumentation (1985), 21 163-70.

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## Appendix

### Appendix I Chemicals tested, abbreviations and notes.

Chemical and abbreviation	Comments
Benzenedimethanol (BDM)	
Benzonitrile (BN)	
Benzthiozole (BT)	
Butyric Acid (BA)	
Carbontetrachloride (CT)	
Chloroform (Chfm)	
Ethylhexanol (EthHex)	
Ethyltoluene (ET)	
Freon 114 (F114)	In Methanol
Freon 12 (F12)	In Methanol
Freon 11 (F11)	In Methanol
Heptane (Hept)	
Hexamethenetramine (HMT)	
Methanol (MeOH)	
Methyldisulfide (MDS)	
Methylnaphthalene (MN)	
MethylPentane (MP)	
Nonylaldehyde (NA)	
Pseudoscent 1 (PS1)	Proprietary mix used to train dogs in cadaver search.
Pseudoscent 2 (PS2)	Proprietary mix used to train dogs in cadaver search.
Pseudoscent drowning (PSD)	Dissolved in water
Tetrachloroethylene (4ClEthy)	
Trichloroethylene (3ClEthy)	In Methanol
Undecane (UN)	
Valeric Acid (VA)	
Xylene (XY)	