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Electronic Aroma Detection Technology for Forensic and Law Enforcement Applications

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ABSTRACT

A major problem hindering criminal investigations is the lack of appropriate tools for proper crime scene investigations. Often locating important pieces of evidence means relying on the ability of trained detection canines. Development of analytical technology to uncover and analyze evidence, potentially at the scene, could serve to expedite criminal investigations, searches, and court proceedings. To address this problem, a new technology based on gas sensor arrays was investigated for its applicability to forensic and law enforcement problems. The technology employs an array of sensors that respond to volatile chemical components yielding a characteristic "fingerprint" pattern representative of the vapor-phase composition of a sample. Sample aromas can be analyzed and identified using artificial neural networks that are trained on known aroma patterns.

Several candidate applications based on known technological needs of the forensic and law enforcement communities have been investigated. These applications have included the detection of aromas emanating from cadavers to aid in determining time since death, drug detection for deterring the manufacture, sale, and use of drugs of abuse, and the analysis of fire debris for accelerant identification. The results to date for these applications have been extremely promising and demonstrate the potential applicability of this technology for forensic use.

Keywords: aroma detection, sensor technology, polymer sensor array, neural network, forensic applications, drugs, accelerants, time since death

1. INTRODUCTION

Aromas are mixtures of volatile organic chemicals; each vapor sample may contain hundreds of volatile components. The key to aroma detection is not to monitor individual chemicals but to have an array of sensors able to respond to a large number of different chemicals. The goal of an aroma detector is to ensure that every component in a vapor is detected by at least one sensor so that each vapor sample gives a characteristic fingerprint from the sensor array. This is the basic operating principle behind some recently developed devices called "electronic noses".[1,2] It is our belief that these devices can be used in forensic and law enforcement applications where trained canines are generally employed.

Canines are used in a number of aspects of forensic investigations such as the detection of drugs, explosives and accelerants and in search and rescue/recovery efforts. The limits of a dog's sense of smell, however, have yet to be defined and the actual components of an aroma that cause an alerting response are generally not known.[3] Because of this, the reliability of search dogs is often questioned and the evidence produced from a successful search inadmissable in a court of law. What is known about the

canine olfactory system is that odor detection occurs in the nasal cavity on a mucus-covered membrane called the sensory mucosa.[3] One theory for scent detection is the "lock and key" theory which states that each scent has a different shape which must fit within a scenting cell of the corresponding shape to be registered by the brain.[4] After a scent molecule is accepted by a scenting cell, the impulse is sent to the brain for identification.

The detection mechanism of the electronic devices mimics these main aspects of the canine (and human) olfactory system: sensing, signal processing, and recognition.[1-3] A vapor sample is introduced across an array of sensors where each sensor within the array exhibits a change in electrical resistance upon interaction with the volatile components. Recognition and identification can then be achieved using an artificial neural network. As in canine training, identification by the neural network is only as good as the training set (i.e. the more data that is presented, the more discriminating the instrument becomes). Despite the similarities between trained canines and the electronic noses, aroma detection technologies have not yet been implemented in forensic or law enforcement work. The objective of this work is determine those applications in which aroma detection technology may be used to supplement the work of canines, to provide information at scene, and to determine the suitability for field use.

2. EXPERIMENTAL

The instrument used in this evaluation was the AromaScanner (AromaScan, Inc.,Hollis, NH). The device operates using an array of sensors that respond to different volatile (and semi-volatile) chemicals to yield a unique "fingerprint" for each vapor sample. The AromaScanner detects the composition of an aroma using an array of 32 electrically conducting, organic polymer sensors. An inking or masking process is used to put the polymer sensors on a single computer chip or board. The organic polymers are based on heterocyclic compounds, such as aniline and pyrrole, and are sensitive to the steric, ionic, hydrophobic and hydrophilic variations of a sample. Adsorption and subsequent desorption of volatile chemicals at the polymer surface causes temporary changes in electrical resistance. The kinetics of the reversible adsorption and desorption processes occur rapidly at room temperature.

2.1 Sample handling

The variables that can affect a change in sensor response, temperature and humidity, need to be precisely controlled to achieve consistent results. This is accomplished by adjusting the temperature and humidity of the reference air and by conditioning the sample under the same conditions prior to analysis. The AromaScan Sample Station incorporates an incubator to provide a constant temperature (35°C) and a humidifier to adjust the water content (absolute humidity) of the reference air. Since the sensors zero themselves during the calibration part of the data acquisition process it is important to ensure that the reference air has a similar humidity to the sample. Matching the humidity of the reference air to that of the sample tends to reduce the effect of water and enhances the volatiles in the vapor phase of the sample.

The two sampling techniques used with the AromaScanner are equilibration and dynamic stripping. Equilibration is generally used when the characteristic compounds of the aroma are more volatile. In this technique, the sample is placed in a disposable sealed pouch (capacity ~500 mL), filled with reference air, and allowed to equilibrate in the Sample Station. During the equilibration period, the volatiles accumulate in the headspace which is then drawn from the pouch and pulled across the sensors.

Dynamic stripping is reserved for samples that are wet or have aromas of lower volatility. In this technique, the headspace does not need to equilibrate because it is constantly being replenished with the conditioned reference air. Samples are placed in bottles (capacity ~500 mL) for dynamic stripping and short lengths of PTFE tubing are used to connect the inlet and outlet ports to the reference air and sensor array, respectively.

2.2 Data acquisition

Acquisition methods consist of a four-step sequence of actions to transport the headspace from the sample across the sensors. Depending on the requirements of the sample, step sequence and duration can be programmed using the software. Each step in the sequence represents a change in valve state that controls the flow of air across the sensors. A typical valve sequence and duration is: reference (0.5 min), sample (2.0 min), wash (1.0 min), and reference (1.5 min). In the first sequence, reference air is sampled to give a stable baseline reading. The headspace from the sample is then introduced in the second sequence. A sampling time is chosen such that the sensor response has equilibrated during that interval. Volatiles are removed from the sensors during the wash sequence. A wash solution of 2% butanol in water is typically used. The final valve sequence is generally reference air to remove any remaining wash vapors and to allow the sensors to re-stabilize.

2.3 Data processing

After acquisition of the raw data, data manipulation software is used to develop databases characteristic of a specific aroma. This is done by selecting the region of data with the smallest deviation in pattern. The regions of greatest instability are those at the start and end of the runs. These are generally not used. The selected region is added to the database in slices representing segments of five seconds each over the time interval selected.

The databases can then be mapped to provide a pictorial representation, or AromaMap, of pattern similarity or difference. The AromaMap is a multi-dimensional compression of the data into a 2-dimensional plot defining the magnitude of the sample aroma differences by distance and direction. The statistical technique is based on Sammon Mapping.[5] The AromaMap can be used to check the similarity between known and unknown data for initial classification and to provide a means of assessing data patterns used for neural network training. For example, if two patterns overlap, the neural network will have difficulty in distinguishing them. Measurement of the Euclidian distance between aroma patterns of different samples provides a quantifiable indication of the difference between two samples. The higher the Euclidian distance, the greater the difference in aromas.

Databases can also be used to train the artificial neural network software so that specific aromas can be identified. The training process used by the software is known as supervised feed-forward using a three-layer network. The pattern recognition technique used is fuzzy-back propagation. The neural network is trained using selected descriptor databases. The database name is used by the neural network as the global classifier description and the data slice name is used as the descriptors for subclassifiers. Once trained and validated, the neural network can be used to provide real-time aroma identification during data acquisition or can be used for classification of database files.

3. RESULTS AND DISCUSSION

Several candidate applications based on known technological needs of the forensic and law enforcement communities have been evaluated using electronic aroma detection technology. These applications included drug detection for deterring the manufacture, sale, and use of drugs of abuse, cadaver decomposition research for determining time since death, and arson investigation for identifying accelerants in fire debris. The preliminary results obtained for each of these applications will be described, as well as recommendations for continued research and related future applications.

3.1 Drugs

Drug standards were analyzed using the equilibration technique and by direct sampling out of the actual drug containers. Equilibration time was 30 minutes at 35°C. For direct sampling analysis, the drug containers or bottles were held directly under the sniffing port of the analyzer. The drugs analyzed included cocaine (1 g), opium (5 g), marihuana leaf (1 g), morphine sulfate (50 mg), amphetamine (100 mg), heroin hydrochloride (5 g), and pseudo scent formulations for cocaine, marihuana, and heroin. The reference air humidity was set to 1.0 g/m^3. The method used for analysis was reference (0.5 min), sample (2 min), 2% alcohol wash, and reference (1.5 min).

Pure drug standards were analyzed using the equilibration method and by sniffing the contents directly out of the bottle. For most of the drug standards analyzed, little response relative to the reference air was observed using either sampling technique. This may be a result of the low vapor pressure[6] of these chemicals, not using enough material in the analysis, or the use of pure drug standards rather than street drugs which are known to have trace impurities. Distinctive fingerprints were obtained for the heroin and opium samples and the patterns were reproduced with either sampling technique. The fact that fingerprints were obtained for these two drugs may be due to the higher amounts of drug (5 g) used in the analysis relative to the amounts used for the other drugs ($\leq$1 g). In addition to the drug standards, three pseudo drug scents, cocaine, marihuana, and heroin were also analyzed. These formulations, developed by Sigma Chemical Co., are used for training drug detection dogs. As for the cocaine and marihuana drug standards, the corresponding pseudo scents did not show characteristic patterns. The pseudo formulation for heroin did produce a weaker but somewhat characteristic fingerprint. The normalized sensor response for heroin (thick line) and the pseudo heroin scent (thin line) are shown in Figure 1. Results are shown for the average of two analyses. Although this pseudo formulation is used as a canine training aid, it is interesting to note that the electronic nose indicates that the two sample aromas are somewhat different.

The fact that poor responses were observed for the majority of drugs suggests that further work needs to be performed to determine the cause of the problem. It may be determined that the vapor pressures of these compounds are too low to produce an appreciable "aroma" or that lengthy equilibration times are needed making this technology unsuitable for remote drug detection. An alternative use may be for detecting product tampering or for the detection of trace manufacturing impurities such as the volatile solvents used in production processes.

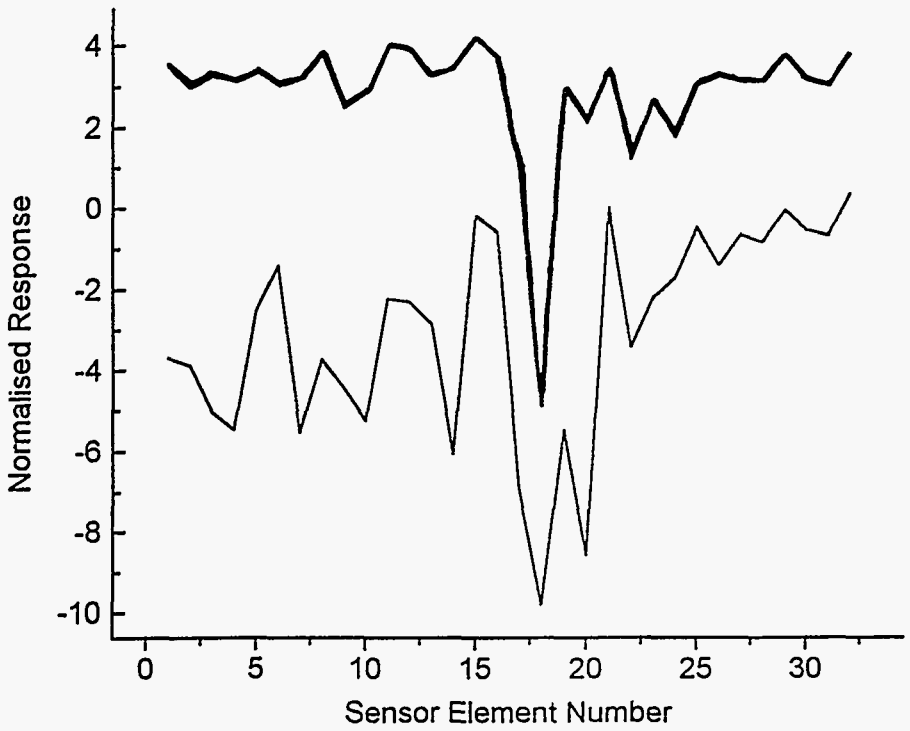

Figure 1. Sensor response for heroin (thick line) and pseudo heroin scent (thin line).

3.2 Time since death

Samples consisted of soil specimens collected from underneath cadavers in various stages of decomposition. An aliquot (1 g) of the soil collected was diluted by adding 10 g of sand and 5 mL of water to create a slurry. A 10 µL aliquot of this slurry was pipetted into a sample pouch. Samples were analyzed using the equilibration technique with an equilibration time of 30 minutes at 35°C. The absolute humidity of the reference air was set at ~8.0 g/m^3. The method used for analysis was reference (0.5 min), sample (2 min), acetone wash (1 min), and reference (6.5 min).

Despite the fact that trained canines can detect human versus animal remains even after several years of decomposition, little is known about the aroma emanating from a corpse. The odor of death is extremely characteristic and pungent consisting of a multitude of volatile chemicals including, phenols, sulfides, indoles, and fatty acids. An understanding of decomposition chemistry may lead to better canine training methods, complementary instrumentation for search and recovery, and determination of forensically important information such as time since death.[7] It is the latter application that was investigated using the AromaScanner. Soil samples collected from beneath different cadavers were analyzed using the equilibrium technique. The samples were acquired from a hispanic male (HM), a

white female (WF), a white male (WM), an unknown corpse (UNK), a dog, and a control soil (CTRL). The fingerprints for each of the samples were easily distinguished (Figure 2). The numbers indicate the date the sample was taken.

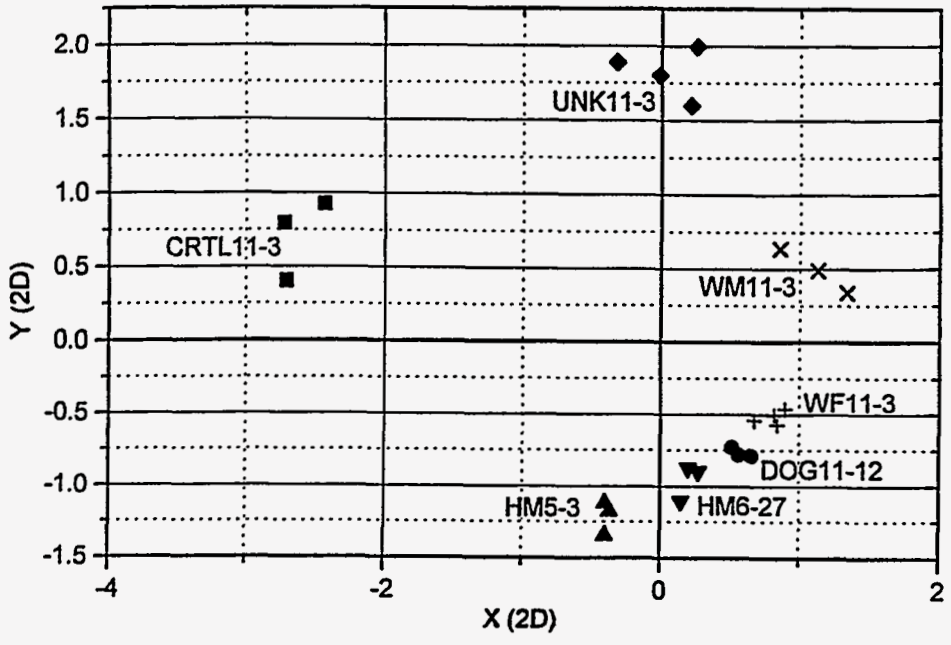

Figure 2. AromaMap of cadaver soil samples.

These results bring up the question - why are the fingerprints different? By looking at the actual sensor response for each of the cadaver samples, it is obvious that the fingerprint patterns are virtually the same. The Euclidian distances between the samples are very small (0.354 to 2.249) indicating that the aromas are similar. This can be seen by looking at the actual sensors response for the soil samples, Figure 3. In this figure, the sensor pattern is reproduced for each of the samples with only slight differences.

The fact that the fingerprint is virtually identical for these samples implies that the aroma is also the same. This suggests that something other than the chemical composition of the aroma is causing the difference in the patterns displayed in the AromaMap. The other factor that can be considered to cause this difference is concentration. This theory was tested by obtaining soil samples from the same cadaver but taken at different days of decomposition. The fingerprint patterns for these samples were taken at 36, 73, 98 days of decomposition. If the actual intensities of these samples are compared without normalizing the sensor response, a clear indication of a concentration effect is seen. This is shown in Figure 4 where the intensity of the sensor response increases with increasing decomposition interval.

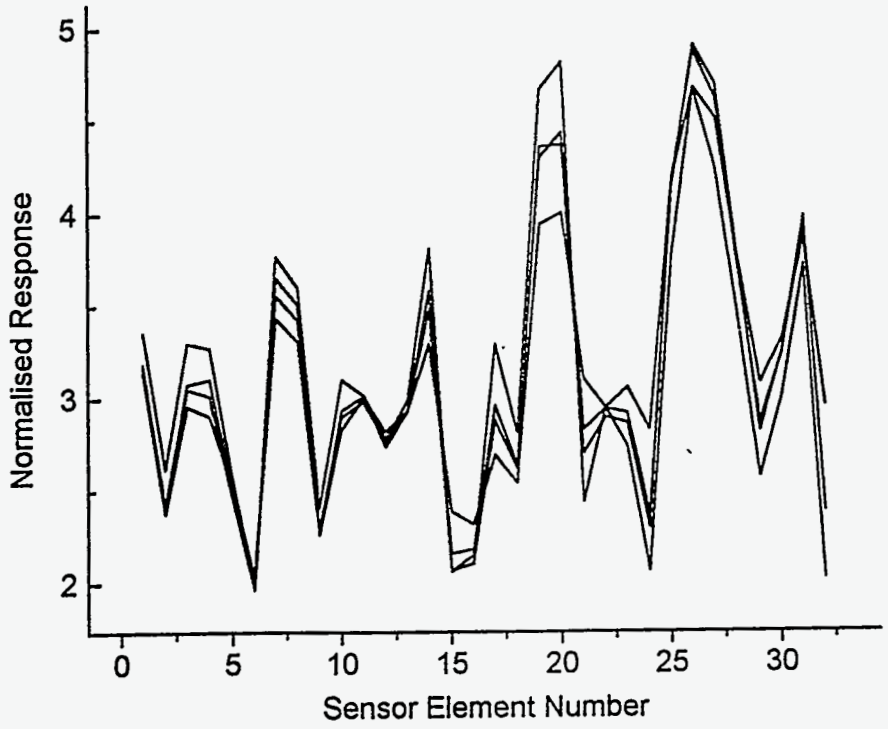

Figure 3. Sensor response for soil samples taken from different cadavers.

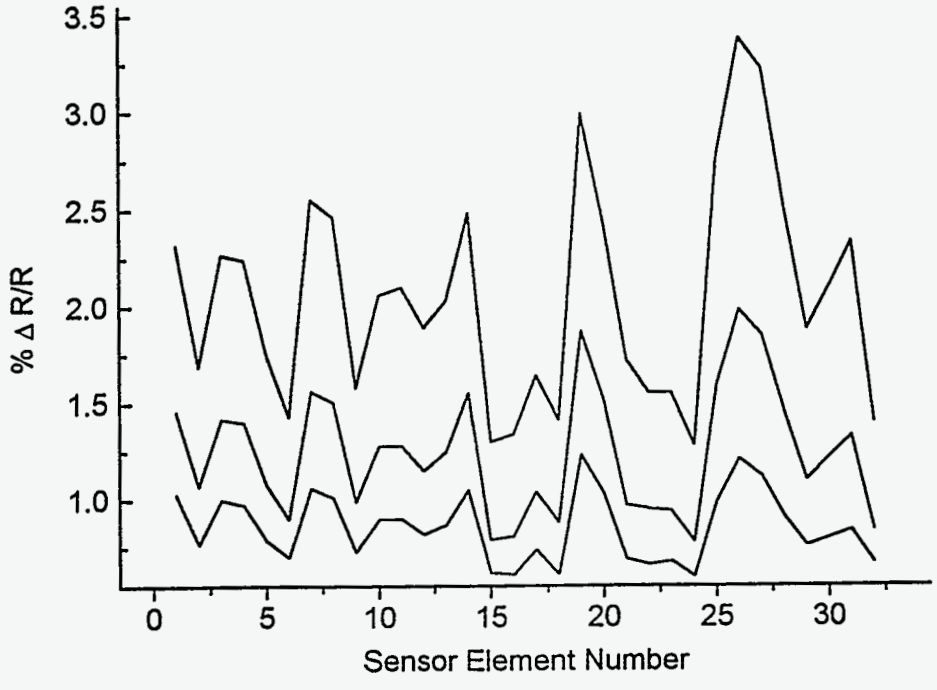

Figure 4. Sensor response as a function of decomposition interval. (bottom = 36 days, middle = 73 days, top = 98 days)

If the Euclidian distances between the control and the cadaver soil samples are plotted, Figure 5, a correlation can be seen relating to the decomposition interval (converted to accumulated degree days which account for average daily temperatures). This information with further time points may prove useful as a means of determining time since death.

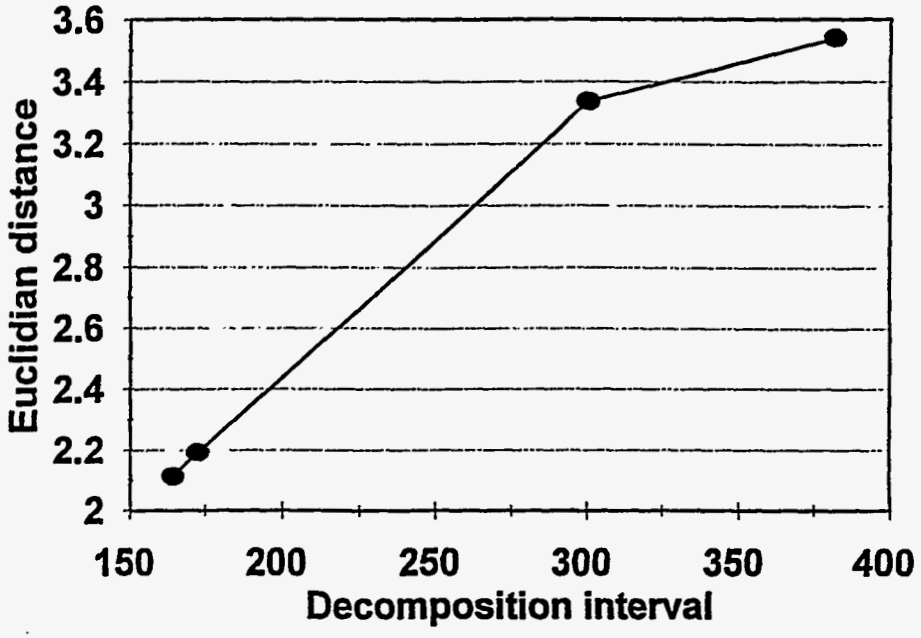

Figure 5. Euclidian distance versus decomposition interval.

3.3 Accelerants and fire debris

Accelerants and residues were analyzed using the equilibration method. Fire debris and accelerant residues were collected from a controlled burn of an abandoned house. Aliquots of neat accelerant (1-2 L) were spread across a 1-2 ft area of carpeting and ignited. After a burn period, the fire was extinguished and samples were collected in sample pouches and paint cans. Neat accelerants (100 μL) or fire debris samples (~10 g) were placed into sample pouches and allowed to equilibrate at 35°C for 30 minutes prior to analysis. The reference air humidity was set to ~7.0 g/m^3. The method used for analysis was reference (0.5 min), sample (2 min), 2% alcohol wash (1 min), and reference (1.5 min).

The use of chemical sensor arrays and neural networks has been applied to the analysis of automotive fuels.[8] This study was performed to expand upon that work and to determine the applicability of the technology for the analysis of fire debris. The accelerants tested as neat chemicals included gasoline, kerosene, mineral spirits, lacquer thinner, motor oil, and diesel fuel. An AromaMap of the resulting databases for the neat chemicals indicated that all were distinguishable except mineral spirits and kerosene which showed some overlap in pattern. Two separate analysis at 100 μL and 10 mL of neat chemical were unable to detect appreciable differences in the fingerprints of these two chemicals under the conditions used. These results are shown in the AromaMap in Figure 6.

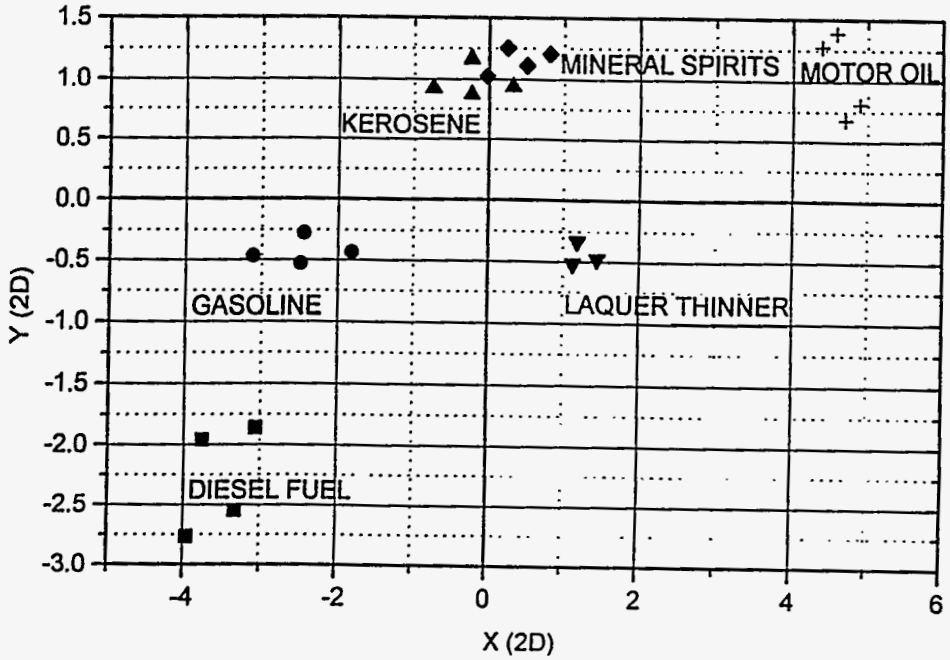

Figure 6. AromaMap of neat accelerants.

Fire debris samples containing gasoline, kerosene, and diesel fuel residues were analyzed to determine the effect of burning on the fingerprint pattern. Analysis of the accelerant residues showed different fingerprint patterns for all the residues tested. The resulting patterns were also shown to be different from the patterns of the neat accelerants. AromaMaps of each accelerant showed no overlap for the control, a weak and strong residue, and the neat chemical. An example AromaMap is shown in Figure 7 for gasoline.

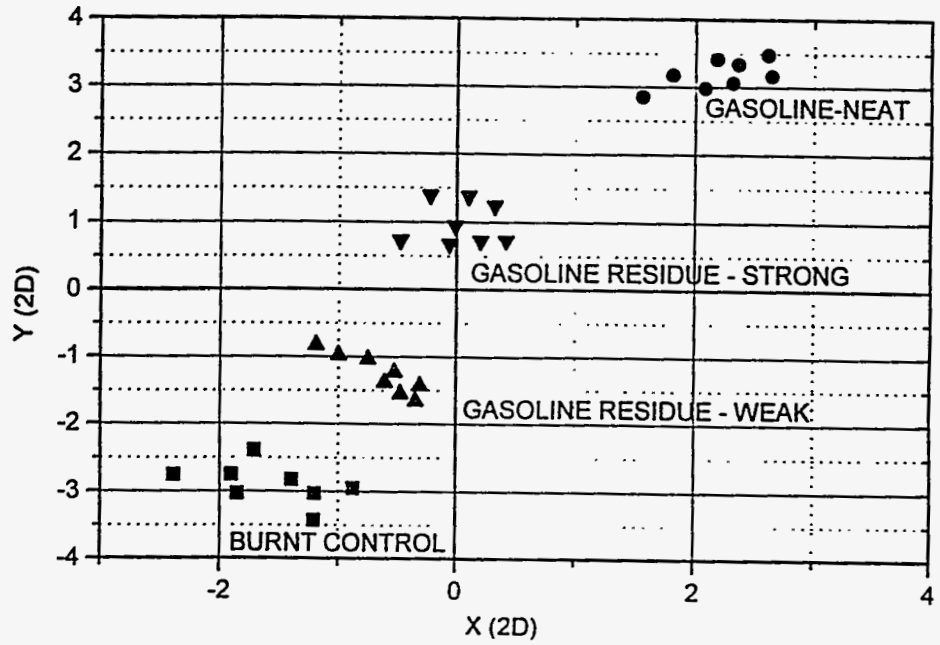

Figure 7. AromaMap of gasoline samples.

The databases for the neat accelerants and known fire debris samples were then used to train the neural network. Each accelerant (gasoline, kerosene, and diesel fuel) was used as a global classifier and the subclassifiers were neat, strong residue, and weak residue. Unknown fire debris samples that had been collected in paint cans were transferred to sample pouches (2 pouches per sample were prepared), analyzed, and classified using the trained neural network. The samples corresponding to diesel fuel were classified with the correct global class and the subclass varied between weak and strong residue. The samples corresponding to gasoline and kerosene, however, were incorrectly classified as diesel fuel or unknown. It is believed that the incorrect classification was due to the much higher humidity of the unknown samples relative to the samples used to train the neural network. To test this theory, drierite was added to the unknown samples in an attempt to remove the excess water. Re-analysis of the unknown samples showed no decrease in sample humidity and no change in sample classification. The drierite was also analyzed by placing it in a sample pouch and allowing it to equilibrate. Both unknowns corresponding to kerosene were identified with the correct global class and with a subclass of weak residue. The unknown samples corresponding to gasoline were also classified with the correct global class and a subclass of either neat or strong residue. The sensor response for the strong gasoline residue sample (thick line) and the unknown sample (thin line) are shown in Figure 8 and for neat gasoline (thick line) and the drierite (thin line) used to dry the unknown sample in Figure 9.

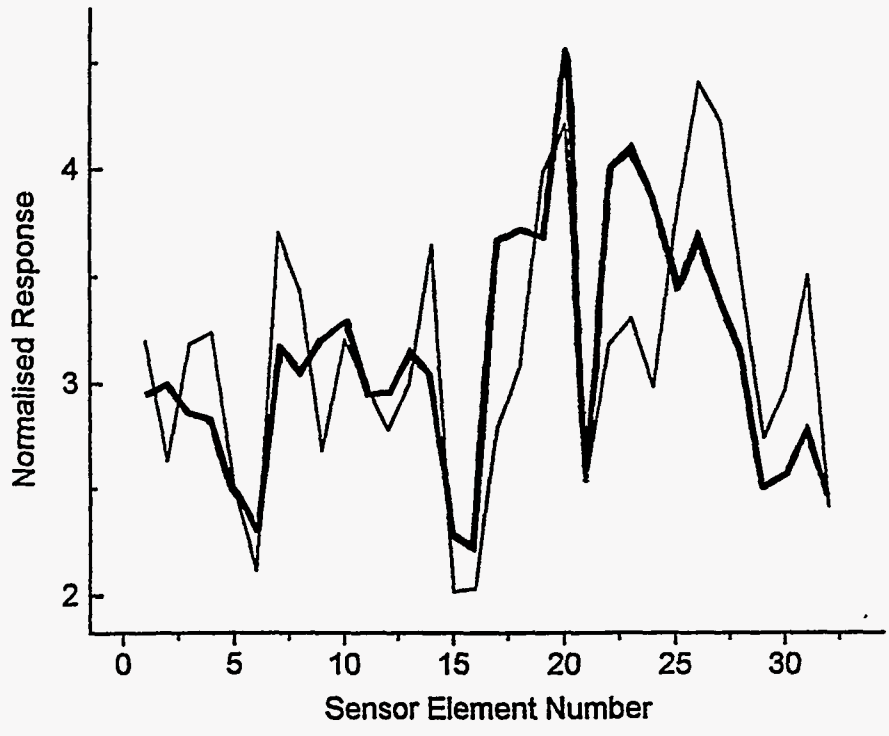

Figure 8. Sensor response for gasoline residue (thick line) and the corresponding unknown sample (thin line).

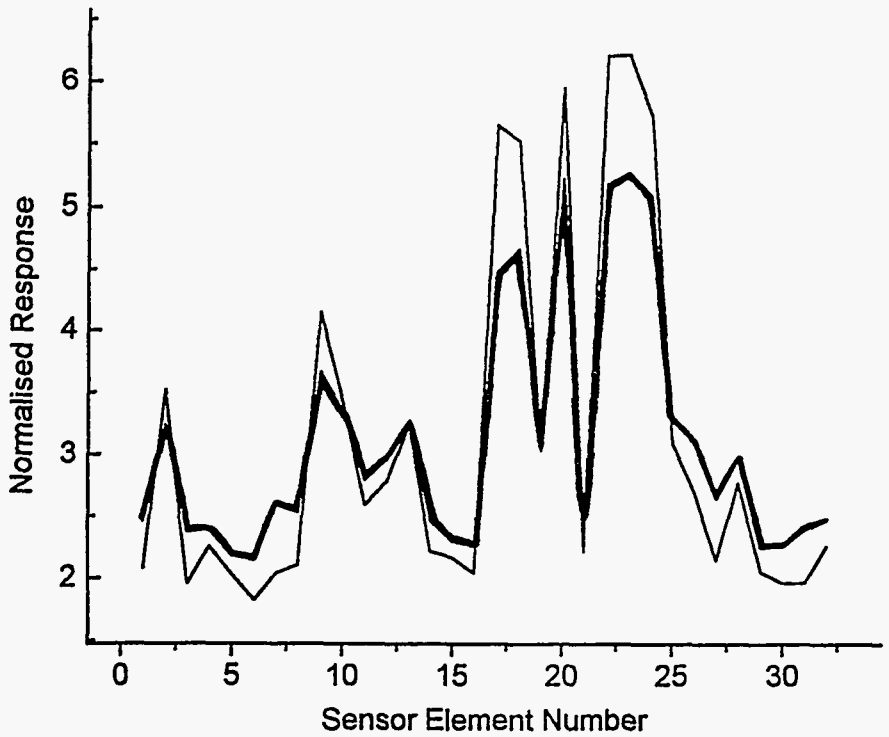

Figure 9. Sensor response for neat gasoline (thick line) and drierite sample (thin line).

4. CONCLUSIONS

Preliminary results for the applications evaluated were quite promising. Further work will be necessary to define fully the utility of aroma detection technology for law enforcement work. In this study it was found that most of the pure drug standards analyzed did not have sufficient vapor pressure for this technique. Aroma detection technology, however, may be useful in related drug applications such as detecting product tampering or manufacturing impurities. The results for the time since death study were extremely promising. A correlation was found by measuring the Euclidian distances between the control and the decomposition samples and plotting this versus the decomposition interval. Further sample points will need to be taken to understand fully this potential correlation and its relation to estimating time since death. The arson work is the most complete to date and the results have been extremely promising. The main problem to overcome is the issue of humidity. To eliminate this problem, the sample introduction technique needs to be addressed. The preliminary work done with sorbent sampling may be the answer to this problem.

5. ACKNOWLEDGMENTS

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