CONF-970659--1

prepared for submission to:

Journal of Forensic Sciences

January 17, 1997

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FEB 12 1997
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Analysis of Accelerants and Fire Debris using Aroma Detection Technology

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* Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp., U.S. Department of Energy under contract DE-AC05-96OR22464.

Running head or foot line: Aroma Detection Technology for Arson

DISCLAIMER

ABSTRACT: The purpose of this work was to investigate the utility of electronic aroma detection technologies for the detection and identification of accelerant residues in suspected arson debris. Through the analysis of known accelerant residues, a trained neural network was developed for classifying suspected arson samples. Three unknown fire debris samples were classified using this neural network. The item corresponding to diesel fuel was correctly identified every time. For the other two items, wide variations in sample concentration and excessive water content, producing high sample humidities, were shown to influence the sensor response. Sorbent sampling prior to aroma detection was demonstrated to reduce these problems and to allow proper neural network classification of the remaining items corresponding to kerosene and gasoline.

KEYWORDS: forensic science, accelerants, fire debris, arson, aroma detection, gas sensor arrays, artificial neural network

Arson is defined as the malicious burning of or attempt to burn property. The goal of arson investigations is to determine whether there is evidence at the scene to indicate that the fire was deliberately set. Of primary interest to the investigation is the cause (nature of the accelerant and source of ignition used) and origin of the fire. Suspicious fires are those that have multiple origins, suspicious burn patterns, an unusually high rate of spreading, or visible remnants of an ignition device (1). When such evidence points toward a fire deliberately set, the investigator must then search through the fire debris for physical evidence to support their suspicions.

A variety of analytical methods have been used for the chemical analysis of fire debris. The analytical challenge in analyzing fire debris is establishing the presence of trace accelerant residues in a background of pyrolyzed material. The main areas of concern to the analyst include: sample preparation, analysis, and data interpretation. Sample preparation techniques for the chemical analysis of suspected arson debris have recently been reviewed (2). Generally, these methods can be divided into the following categories: direct (or static) headspace (3), passive (4,5) and dynamic (6,7)] headspace, distillation, and solvent extraction (8). Several of these techniques have been adopted by the American Society for Testing and Materials (ASTM). A new sampling method, solid phase microextraction (SPME), has also recently been introduced (9,10). This is a passive headspace extraction method that incorporates a sorbent-coated silica fiber as the sampling medium and utilizes thermal desorption elution.

Sample analysis is typically performed using gas chromatography. The ASTM method uses gas chromatography and allows for a variety of detectors including flame ionization, photoionization, and mass spectrometric (11). The reported detection levels are 0.1 to 10 μL for petroleum products and liquid residues. The major problems associated with chromatographic methods are the complexity of the chromatograms, the interference of pyrolysates from petroleum-based products, and change in chromatographic profiles due to sample evaporation. Mass spectrometric methods have been employed to simplify chromatograms and to discriminate against pyrolytic interferences (12-16). These methods use extracted ion profiling (mass chromatography) to display the characteristic ions for known classes of compounds as a function of time. The incorporation of macro-programming and expert systems has been investigated to categorize chromatographic profiles automatically (17,18). Despite the widespread use of GC/MS-based methods, intolerably long sample turn-around times are often reported due to lengthy sample preparation, analysis, and data interpretation requirements.

As an alternative to these methods, the ability to classify different accelerants using aroma detection technology was investigated. 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" (19,20). The detection mechanism of the electronic devices mimics the main aspects of the canine olfactory system: sensing, signal processing, and recognition (19-21). Because canines have been trained and used for accelerant detection (22), it is our belief that the electronic devices may equally be applicable to the challenge.

The theory for scent detection is based on a "lock and key" mechanism where each scent molecule has a different shape that must fit within a scenting cell of the corresponding shape to be registered by the brain. After a scent molecule is accepted by a scenting cell, the impulse is sent to the brain for identification. Likewise, 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 trained on known vapor samples. As in training canines for scent discrimination, 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 police dogs and the electronic noses, aroma detection technologies have not been investigated seriously by the forensic or law enforcement communities. It is this author's belief that further experimental data will convince these communities of the utility of this technology and how it can play a complementary role to canine detection programs.

Experimental

Samples - The accelerants used in this study were gasoline, kerosene, mineral spirits, motor oil, diesel fuel, and lacquer thinner. Known accelerant residues and fire debris samples 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 carpet fragments were collected in sample pouches (for use as known accelerant residues) and in paint cans (for use as unknown fire debris samples). Neat accelerants (100 μL), accelerant residues (~10 g), and fire debris samples (~10 g) were placed into sample pouches prior to analysis. Accelerants and samples were analyzed using the equilibration method. In this technique, the sample was placed in the disposable sealed pouch (capacity ~500 mL), filled with reference air, and allowed to equilibrate for 30 minutes at 35°C. The reference air humidity was set to ~7.0 g/m^3.

Sensor array analysis - The instrument used in this study 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. 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.

The method used for analysis was reference air (0.5 min), sample (2 min), wash (1 min), and reference air (1.5 min). Each step in this sequence represents a change in valve state that controls the flow of air across the sensors. In the first step, reference air was sampled to give a stable baseline reading. During the equilibration period, the volatiles accumulated in the headspace which was then drawn from the pouch and pulled across the sensors in the second step. A sampling time was chosen such that the sensor response had equilibrated during that interval. Volatiles were removed from the sensors during the wash step. A wash solution of 2% butanol in water was used. The final step, reference air, was used to remove any remaining wash vapors and to allow the sensors to re-stabilize.

Data manipulation - After acquisition of the raw data, data manipulation software (supplied with the instrument) was used to develop databases characteristic of the specific accelerant and sample aromas. This was done by selecting the region of data with the smallest deviation in pattern. The regions of greatest instability were those at the start and end of the runs. The selected region was added to the database in slices representing segments of five seconds each over the time interval selected. The databases were then mapped to provide a pictorial representation, or AromaMap, of pattern similarity or difference. Databases were then used to train the artificial neural network software so that specific aromas could be identified. The training process used by the software was supervised feed-forward using a three-layer network. The pattern recognition technique used was fuzzy-back propagation. The neural network was trained using selected descriptor databases based on known aroma samples (neat accelerants or accelerant residues). Once trained and validated, the neural network was used to provide classification of database files for the unknown fire debris samples.

Results and Discussion

The ability to differentiate liquid fuels (automotive and aviation) using a simplified chemical sensor array in a neural network-based instrument has previously been reported (23, 24). In this work, only three metal oxide sensors were needed to classify aviation fuels and seven sensors to classify gasoline as to octane rating and the presence of alcohol. Although these were only preliminary findings, the results suggested that the methodology could be used to address other real-world problems. We have investigated the application of an electronic aroma detection device to the real-world problem of arson.

The ability to discriminate accelerants commonly used in arson cases (e.g. gasoline, kerosene, mineral spirits, lacquer thinner, motor oil, and diesel fuel) was determined initially by analyzing the neat chemicals prior to ignition. Fingerprint patterns, based on two replicate analyses, for each of the accelerants are shown in the plots of normalized response versus sensor element number in Figure 1. These data were then used to develop databases for each of the accelerant aromas. The resulting databases are shown in the AromaMap, Figure 2. An AromaMap is a multi-dimensional compression of the fingerprint 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 (25). Measurement of the Euclidian distance between aroma patterns of two aromas can be used to provide a quantifiable indication of the difference between them. The Euclidian distances between each of the accelerants are shown in Table 1. The larger the Euclidian distance, the greater the difference in aromas. Based on this data, most of the neat chemicals were distinguishable with the exception of mineral spirits and kerosene. These two accelerants showed some overlap in the AromaMap, had the most similar fingerprint patterns, and had the lowest Euclidian distance. This problem may be overcome by using alternate sampling conditions. For example, sensor response can be affected by humidity and the intensity of the sensor response can be correlated with temperature, sample concentration, and equilibration time. Additionally, the uniqueness of the fingerprint pattern can be optimized by choosing different regions of the data to assure the most distinct pattern has been selected.

To determine the effect of burning on the fingerprint pattern, accelerant residues (carpet samples containing gasoline, kerosene, and diesel fuel) were obtained from a controlled burn of an abandoned house. Distinguishable fingerprint patterns were obtained for the three residues tested and the control carpet sample. The fingerprint patterns for these samples are shown in Figure 3 and represent eight multiple analyses of each sample. The patterns for the residues were also found to be different from those of the neat accelerants (Figure 1). When graphed 2-dimensionally in an AromaMap, Figure 4, no significant overlap was visible for the control, weak and strong residue samples, and the neat accelerants. Some variability in reproducibility, identified by the loose clustering in the AromaMap, was observed for kerosene in both the neat and strong residue samples. This may be related to inconsistent sampling conditions.

An artificial neural network was set up using the databases created for the neat accelerants and known residues. The databases shown in Figure 4 were used to train the neural network for use in classifying the fire debris samples collected from the controlled house fire. Each of the accelerants (gasoline, kerosene, and diesel fuel) and the control were used as global classifiers. The subclasses were identified as either neat, strong residue, or weak residue. Eight replicate analyses of each sample were used in the training set. The neural network was validated by then re-analyzing the strong residue samples used in the training set and classifying the resulting databases using the neural network. The samples were re-analyzed seven times over a period of 1 to 15 days from the time the neural network training set was originally analyzed. The results are shown in Table 2. The diesel fuel residue sample was classified with the correct global and sub-class for all seven analyses. The gasoline residue was classified with the correct sub-class each time, but incorrectly identified with diesel fuel as the global class 6 out of seven times. It is unclear at this time why these results were obtained. Further training of the neural network may eliminate or minimize this problem. The kerosene residue was classified for both global and sub-class correctly four out of seven times. Only one analysis was mis-identified as unknown for both the global and sub-classes. Six of the seven analyses had kerosene correctly identified as the global class, but two of these had neat rather than strong residue as the sub-class. This is probably a result of a concentration effect that will be discussed further in a following section.

The neural network was further tested by analyzing the unknown fire debris samples from the controlled house fire. Three fire debris samples were collected in paint cans at the site and labeled as items 1, item 3, and item 5. Each paint can or item should have contained one of the three different accelerants used in igniting the fire. Samples were removed from the paint cans and transferred to sample pouches. Two pouches (labeled a and b) per item were prepared, analyzed, and classified using the trained neural network. Eight replicate analyses were performed for each sample. Curiously, all three items (6 samples in total) were predominantly identified by the neural network as diesel fuel. Only item 5b gave an occasional hit as kerosene. Based on the sample humidities monitored during sample acquisition, it was noted that two of the three items had excessively high humidities (≥ 12.0 g/m^3). The humidities of the reference samples used to train the neural network were kept below ~10.0 g/m^3. It is speculated that the excessively high humidities interfered with the sensor response for the analysis of items 1 and 5. With average sample humidities in the correct range, item 3a and 3b were identified as diesel fuel for all eight replicate analyses. This can be seen in the fingerprint patterns shown in Figure 5. Both items 3a and 3b were always classified with the correct global class, diesel fuel, with fits ≥ 91.0 for each analysis. The sub-class for these samples varied between weak and strong diesel fuel residue with fits ranging from 70.0 to 99.0.

Because item 5 was classified as kerosene for two of the eight analyses, it was speculated that other variables besides humidity may have contributed to the missed identifications. Other factors that can influence sensor response are temperature, concentration, and equilibration time.

It is possible that sample 5b produced a hit for kerosene only when sufficient concentrations were present in the headspace or after extensive equilibration times (e.g. after sitting overnight). To investigate these variables, a sorbent material, Drierite®, was added in a vial to the sample pouches containing items 1 and 5. One possible effect of the added Drierite® might be the reduction of the sample humidity by removal of water. The other effect that may be expected from the addition of Drierite® is the concentration of the accelerant vapors on the sorbent material. Activated charcoal strips, for example, are often used in fire debris extractions for passive concentration of accelerant vapors (26). After sitting overnight, the drierite was removed and the samples were re-analyzed. Re-analysis of these two samples showed no decrease in sample humidity and no change in sample classification. Based on these results it appears that the Drierite® was ineffective in removing water from the sample.

The Drierite® itself was then placed in a separate sample pouch, allowed to equilibrate, analyzed and classified using the neural network. Both items 5a and 5b were correctly identified as kerosene. Global class fits for triplicate analyses of these samples were ≥95.8. The sub-class was always identified as a weak kerosene residue with fits ≥96.0. The superimposed fingerprint patterns for kerosene as the neat accelerant, residue, and unknown (item 5), Figure 6a, show good correlation. When the patterns are shown using relative intensities, Figure 6b, the effect of sample concentration can be seen where the neat accelerant is most intense and the unknown, being a weak residue, has the lowest intensity. Although item 1a was correctly classified as gasoline, even with the Drierite® sorbent, item 1b was still occasionally mis-identified by the neural network as either unknown or kerosene. Global class fits for item 1a were 86.1 based on duplicate analyses and for item 1b ranged from 95.3 - 99.8 for correct assignments. The subclassifications for these samples were even more ambiguous ranging from unknown to neat gasoline. Shown in Figure 7 are the fingerprint patterns for item 1b (7c) and the Drierite® used to sample item 1b (7d). These patterns can be compared to those for neat gasoline (7b) and the gasoline residue (7a). Although the neural network had some difficulty in classifying the fire debris corresponding to gasoline (item 1b), the identification of item 1b as gasoline is clearly apparent if the fingerprints for neat gasoline (7b) and the Drierite® sample (7d) are compared. The problems associated with the neural network may reflect the fact that the training set did not include vapors concentrated on a Drierite® sorbent and, therefore, reflect a change in sampling conditions. Since the sorbent results were so promising, future work will include such reference samples in the training set.

Conclusions

The use of aroma detection technology for arson investigation was shown to be feasible. It was determined that the variables affecting a change in sensor response, temperature and humidity, need to be precisely controlled to achieve consistent results. For reference samples, this was accomplished by adjusting the temperature and humidity of the reference air and conditioning the sample at these settings prior to analysis. For actual fire debris samples, however, wide variations in water content were shown to alter the sample humidity and variations in sample concentrations were shown to influence the sensor response. Neural network classifications were often affected because reference and fire debris sampling conditions and sample concentrations were inconsistent. Sorbent sampling prior to aroma detection was demonstrated to reduce these problems and to allow proper neural network classification in some cases. Although the preliminary results were promising, more work remains to be done to understand the relationship between the accelerant, the potential substrate materials, the effect of the fire, and the method of extinguishing the fire and the effects they may have on sampling and sensor response. Further work is necessary to determine the utility of sorbent sampling in conjunction with aroma detection for eliminating the issues of humidity and concentration.

Acknowledgments

The author would like to acknowledge AromaScan, Inc. for the loan of the instrument used to perform this work and for the technical support of this project. The author also thanks the Knox County Fire Investigation Unit for providing samples and technical input.

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Table 1. Euclidian Distances for Neat Accelerants Prior to Ignition

Accelerant	Gasoline	Kerosene	Diesel fuel	Mineral spirits	Lacquer thinner	Motor oil
Gasoline	**1.298***	2.882	5.266	3.708	2.655	6.752
Kerosene	2.882	**1.218**	7.512	1.208	2.459	4.429
Diesel fuel	5.266	7.512	**1.847**	8.461	7.448	11.502
Mineral spirits	3.708	1.208	8.461	**1.139**	2.739	3.592
Lacquer thinner	2.655	2.459	7.448	2.739	**0.797**	4.824
Motor oil	6.752	4.429	11.502	3.592	4.824	**1.355**

* numbers in bold indicate Euclidian distances between replicate analyses of same sample

Table 2. Validation of the Neural Network using the Strong Residue Samples

	Gasoline		Kerosene		Diesel fuel	
Analysis	Global	Sub-class	Global	Sub-class	Global	Sub-class
1	diesel fuel (96.5)*	gas.res.str. (90.7)	kerosene (99.9)	ker. neat (95.5)	diesel fuel (99.9)	dies.res.str. (95.6)
2	gasoline (93.5)	gas.res.str. (96.5)	kerosene (82.3)	ker.res.str. (77.1)	diesel fuel (99.9)	dies.res.str. (98.7)
3	diesel fuel (93.6)	gas.res.str. (95.5)	kerosene (91.0)	ker.res.str. (86.9)	diesel fuel (99.9)	dies.res.str. (99.0)
4	diesel fuel (99.4)	gas.res.str. (97.4)	kerosene (99.9)	ker. neat (91.6)	diesel fuel (100.0)	dies.res.str. (99.1)
5	diesel fuel (99.4)	gas.res.str. (85.6)	unknown (100.0)	unknown (100.0)	diesel fuel (99.9)	dies.res.str. (94.8)
6	diesel fuel (99.0)	gas.res.str. (87.9)	kerosene (98.9)	ker.res.str. (86.9)	diesel fuel (99.9)	dies.res.str. (94.5)
7	diesel fuel (96.0)	gas.res.str. (92.7)	kerosene (96.7)	ker.res.str. (91.1)	diesel fuel (99.9)	dies.res.str. (82.5)

* numbers in ( ) indicate fit

Figure captions

Figure 1. Replicate fingerprint patterns showing normalized response versus sensor element number for six different accelerants: (a) motor oil, (b) kerosene, (c) mineral spirits, (d) diesel fuel, (e) gasoline, and (f) lacquer thinner. Normalized sensor response is equal to ΔR each sensor / ΔR all sensors (where R is the resistance).

Figure 2. A multi-dimensional compression of the neat accelerant fingerprint data into a 2-dimensional plot, or AromaMap, defining the magnitude of the sample aroma differences by distance and direction.

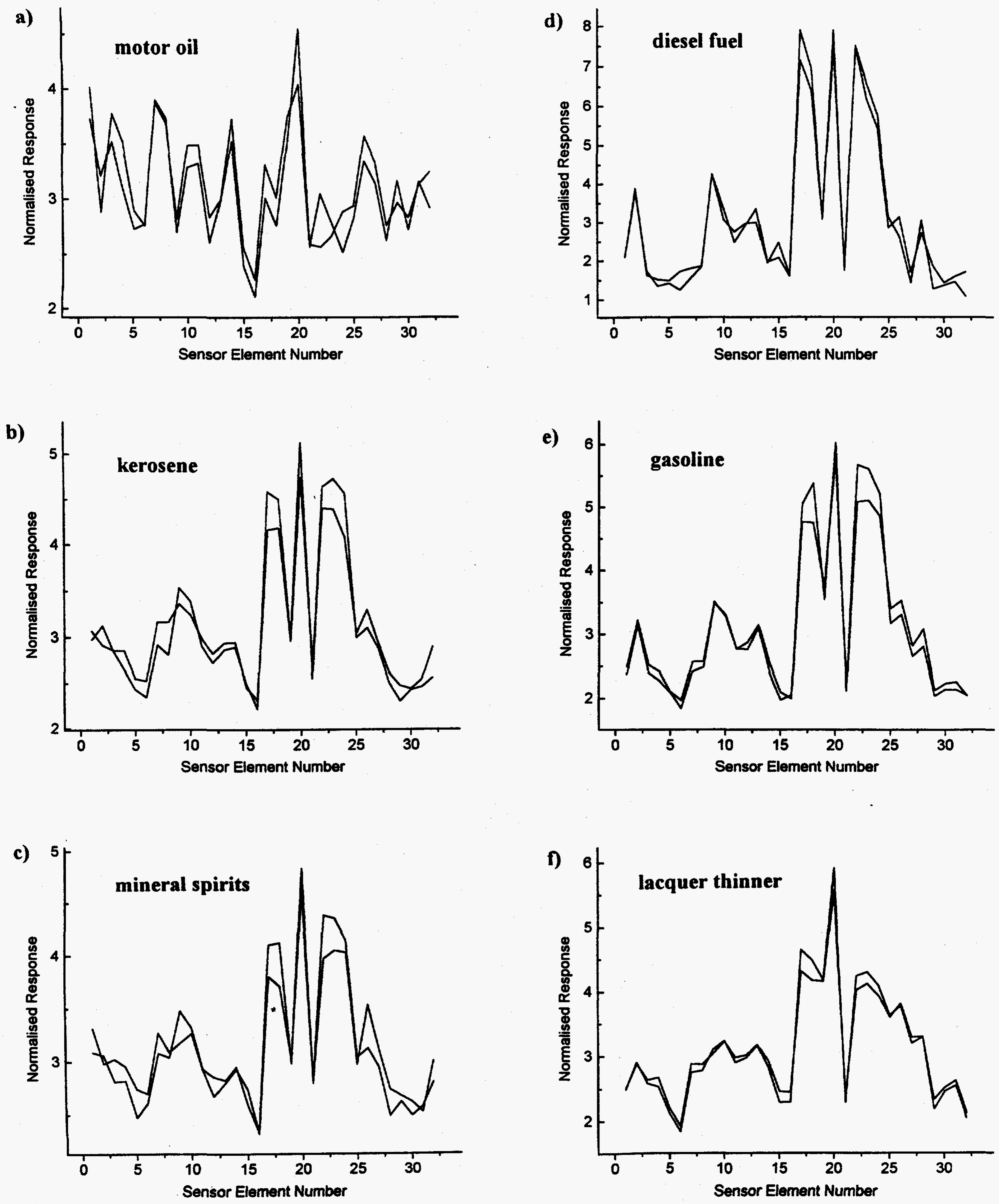
Figure 3. Fingerprint patterns for a control sample (a) and the accelerant residues (b) kerosene, (c) diesel fuel, and (d) gasoline. Residue aromas were obtained from burnt carpeting, padding, wood flooring or combinations of these materials.

Figure 4. AromaMap of the different samples (neat accelerants and residues) used to train the artificial neural network for classifying unknown fire debris.

Figure 5. Fingerprint patterns for the fire debris corresponding to item 3. Both samples 3a (b) and 3b (c) were identified by the neural network as a diesel fuel residue (a).

Figure 6. Superimposed fingerprint patterns for neat kerosene, kerosene residue, and item 5a as normalized data (a) and intensity* data (b). Intensities are determined by ΔR sensor / original R sensor (where R is the resistance).

Figure 7. Fingerprint patterns for gasoline as the (a) residue, (b) neat accelerant, (c) unknown fire debris item 1b, and (d) the Drierite® used to sample item 1b.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Normalised Response
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d)
diesel fuel
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e)
gasoline
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c)
mineral spirits
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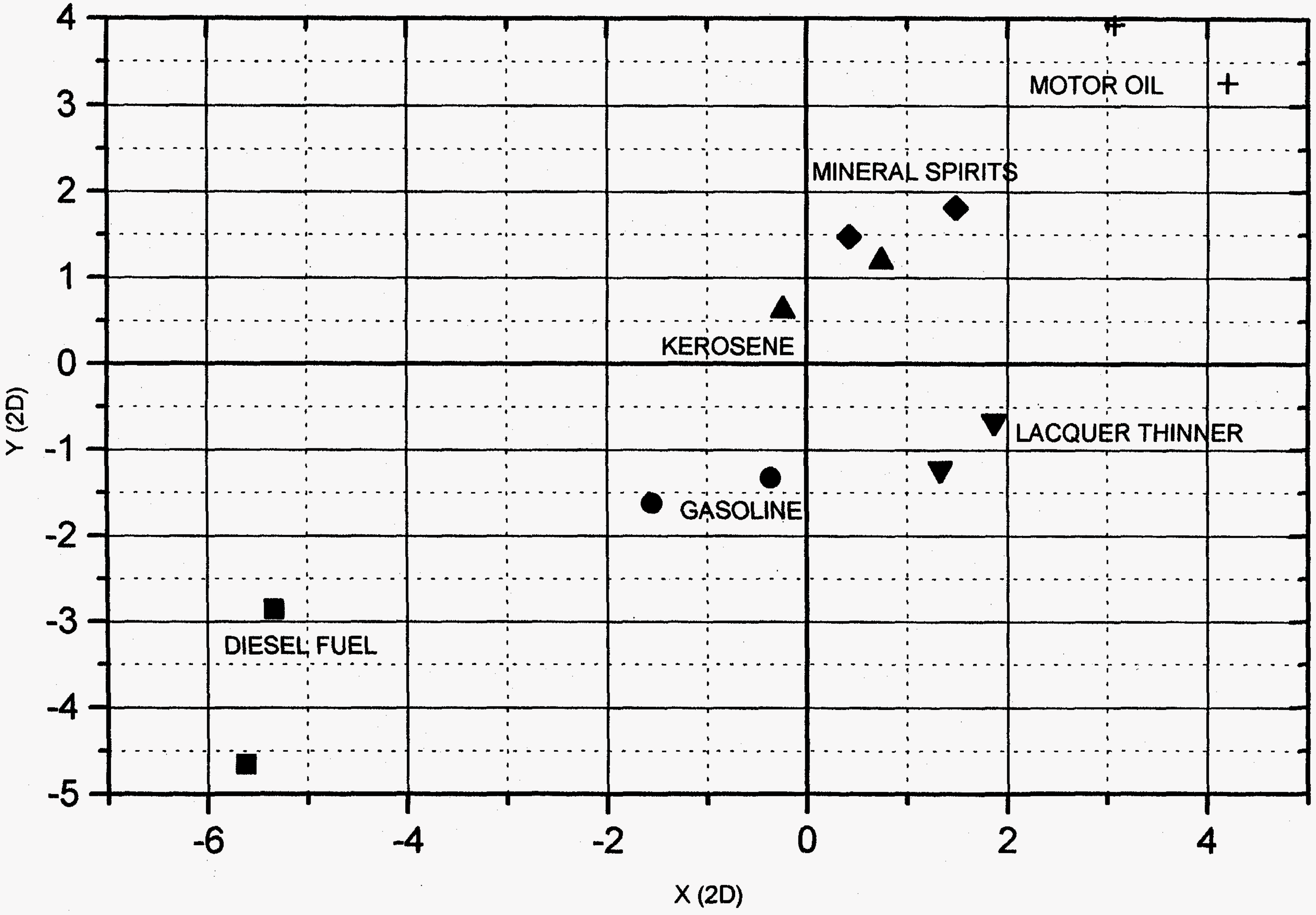
Sensor Element Number



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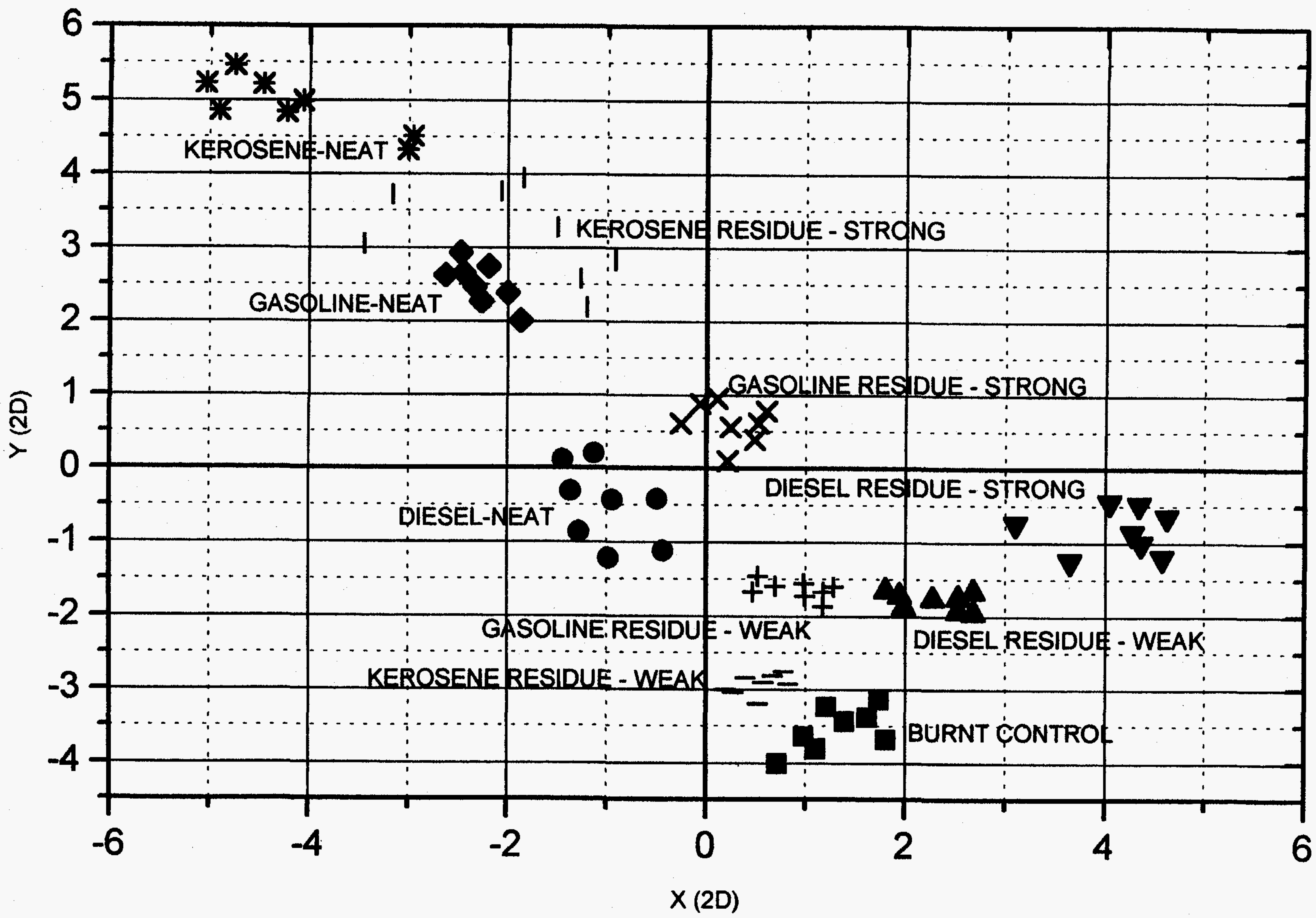
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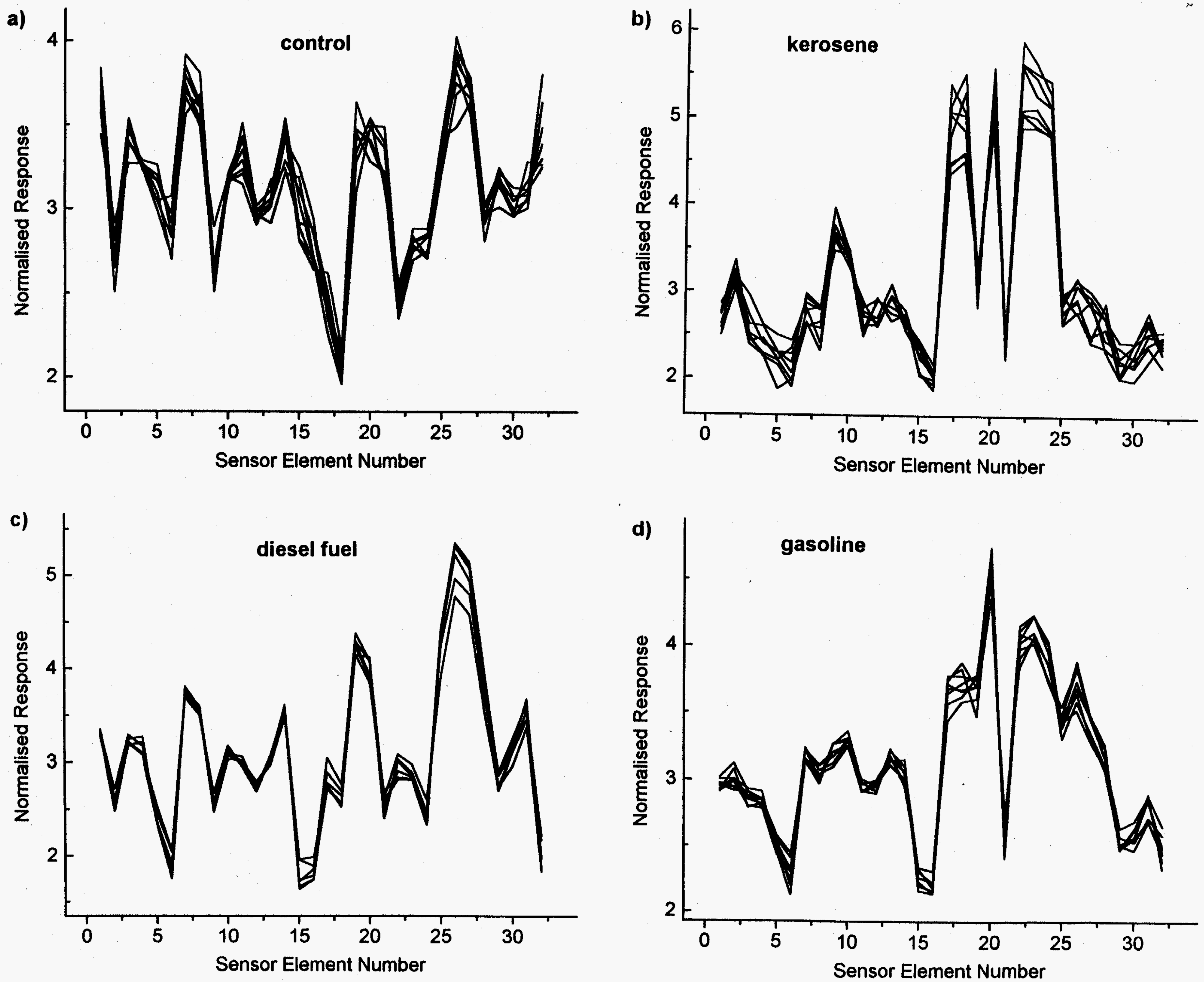
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Normalised Response
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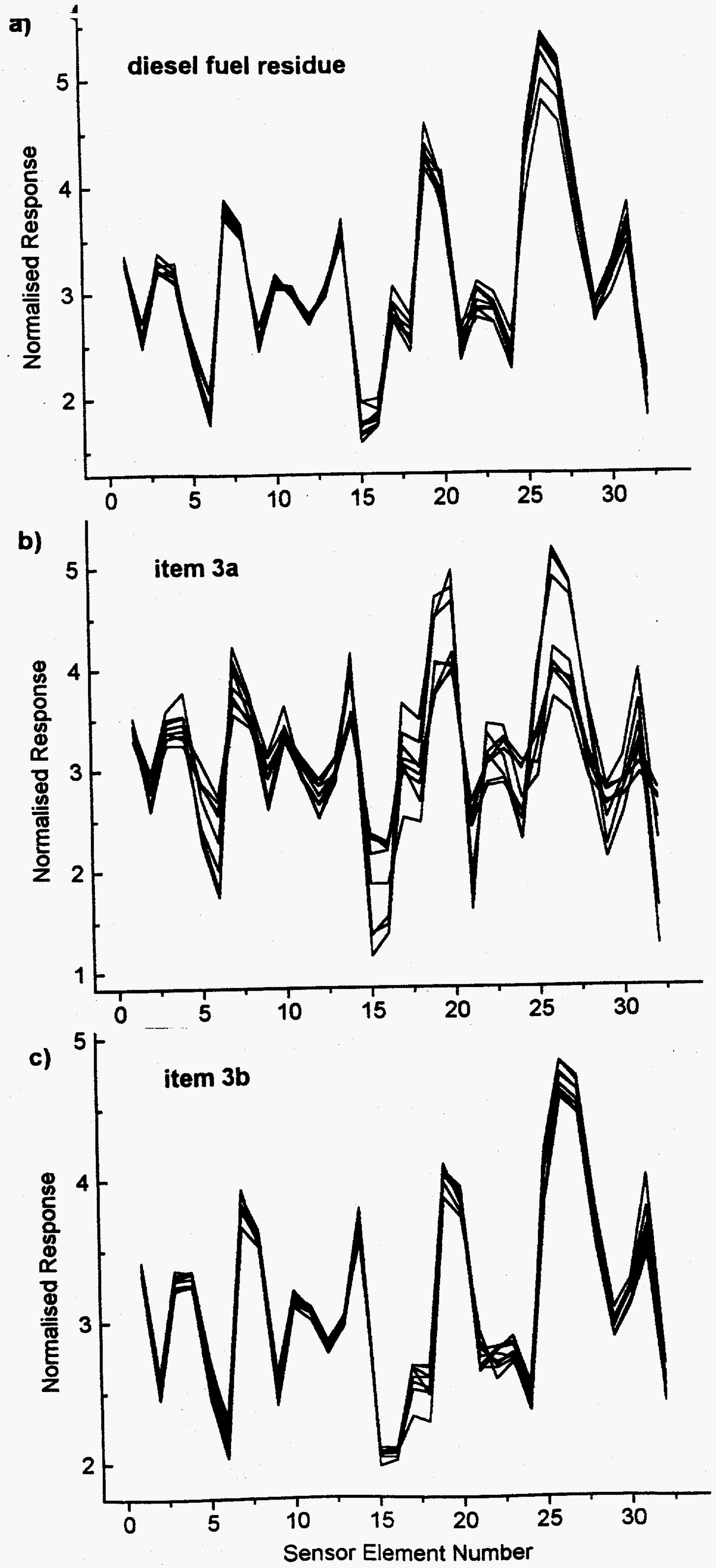
a)
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Normalised Response
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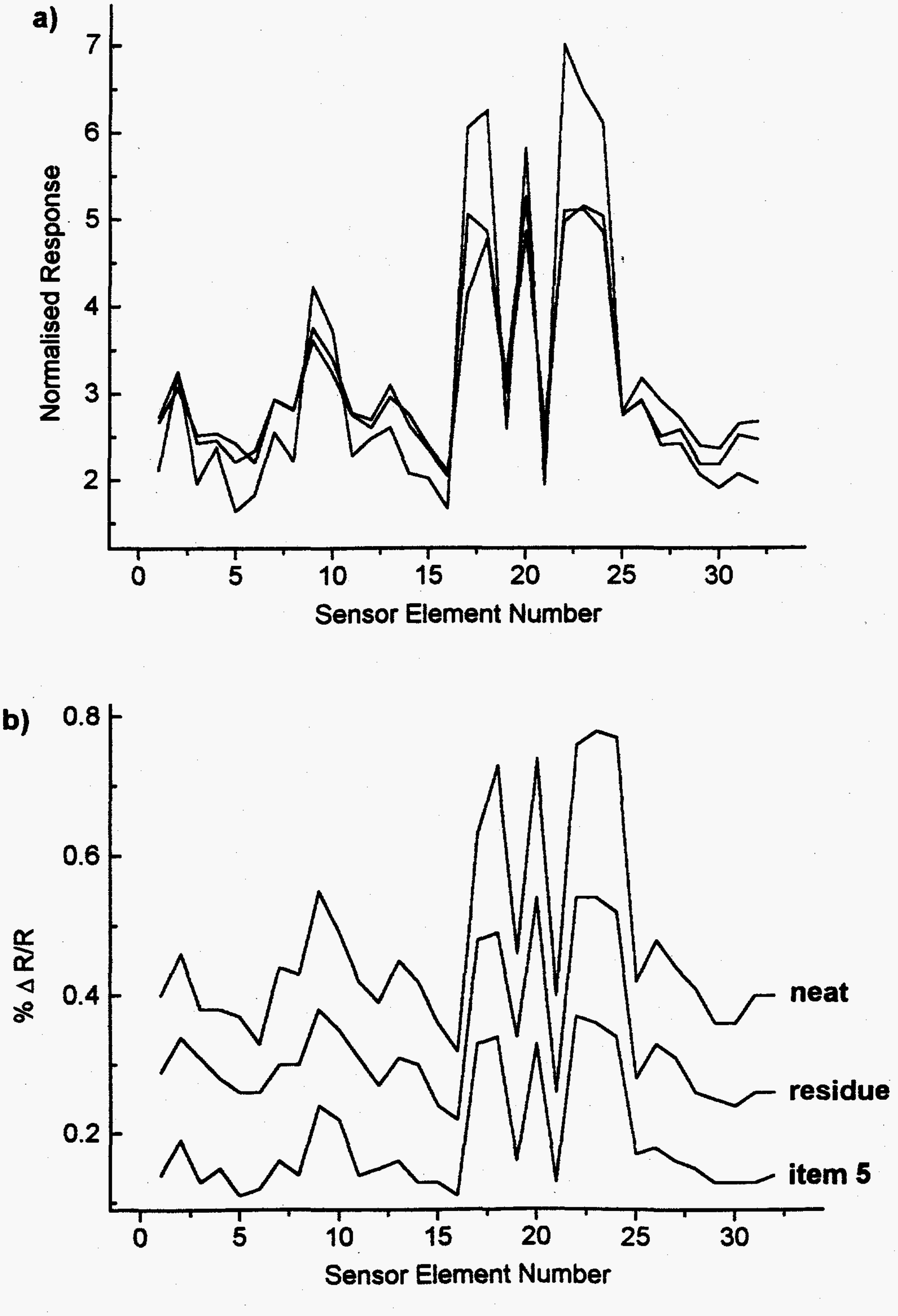
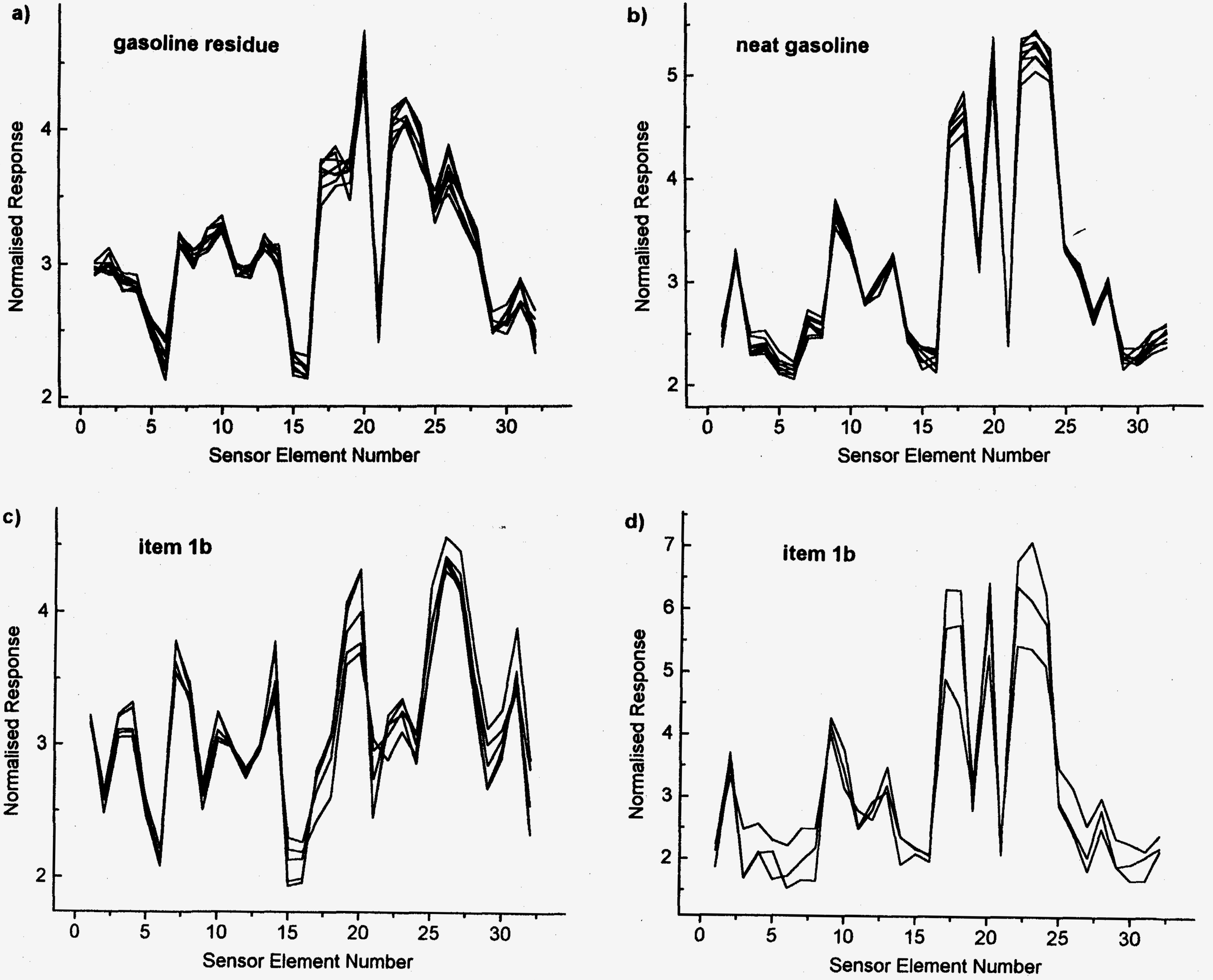
b)
item 3a
Normalised Response
1
2
3
4
5
0
5
10
15
20
25
30
c)
item 3b
Normalised Response
2
3
4
5
0
5
10
15
20
25
30
Sensor Element Number


a)
Normalised Response
2
3
4
5
6
7
0
5
10
15
20
25
30
Sensor Element Number
b)
% Δ R/R
0.2
0.4
0.6
0.8
neat
residue
item 5
0
5
10
15
20
25
30
Sensor Element Number


a)
gasoline residue
Normalised Response
2
3
4
0
5
10
15
20
25
30
Sensor Element Number
b)
neat gasoline
Normalised Response
2
3
4
5
0
5
10
15
20
25
30
Sensor Element Number
c)
item 1b
Normalised Response
2
3
4
0
5
10
15
20
25
30
Sensor Element Number
d)
item 1b
Normalised Response
2
3
4
5
6
7
0
5
10
15
20
25
30
Sensor Element Number