Analysis of Accelerants and Fire Debris Using Aroma Detection Technology

REFERENCE: Barshick SA. Analysis of accelerants and fire debris using aroma detection technology. J Forensic Sci 1998;43(2): 284–293.

ABSTRACT: The purpose of this work was to investigate the utility of electronic aroma detection technologies for the detection and identification of ignitable liquid accelerants and their residues in suspected arson debris. Through the analysis of "known" accelerants and residues, a trained neural network was developed for classifying fire debris samples. Three "unknown" items taken from actual fire debris that had contained the fuels, gasoline, kerosene, and diesel fuel, were classified using this neural network. One item, taken from the area known to have contained diesel fuel, was correctly identified as diesel fuel residue every time. For the other two "unknown" items, variations in sample composition, possibly due to the effects of weathering or increased sample humidities, were shown to influence the sensor response. This manifested itself in inconsistent fingerprint patterns and incorrect classifications by the neural network. Sorbent sampling prior to aroma detection was demonstrated to reduce these problems and allowed improved neural network classification of the remaining items which were identified as kerosene and gasoline residues.

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 this type of investigation is the cause (nature of the solid or liquid 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 or use of an accelerant (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 headspace sampling (3), passive (4,5) and dynamic (6,7) headspace concentration, 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 ignitable liquid 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 the detection of ignitable liquid vapors indicative of accelerants (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

¹Staff scientist, Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp., U.S. Department of Energy under contract DE-AC05-96OR22464.

Received 22 Jan. 1997; and in revised form 17 April, 14 July 1997; accepted 14 July 1997.

where each sensor within the array exhibits a characteristic change in electrical resistance upon interaction with the components of the aroma. 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 characteristic the 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 ignitable liquids used in this study as accelerants were gasoline, kerosene, mineral spirits, motor oil, diesel fuel, and lacquer thinner. These chemicals were initially analyzed as the neat (pure/undiluted) liquid obtained from various commercial sources. "Known" liquid accelerant residue samples and "unknown" fire debris samples were collected from a controlled burn of an abandoned house. Aliquots of the neat liquids (1-2 L) were spread across separated 1-2 ft areas 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 residue samples) and in paint cans (for later use as "unknown" fire debris samples). The neat liquids (100 µL), "known" accelerant residues (~10 g), and "unknown" fire debris samples (~10 g) were placed into sample pouches prior to analysis. All samples were analyzed using the equilibration method. In this technique, the sample (liquid or solid) 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/m³.

Sensor Array Analysis

The instrument used in this study was the AromaScanner Electronic Aroma Detection Device (AromaScan, Inc., Hollis, NH). A block diagram showing the basic operating components of this system is shown in Fig. 1. The AromaScanner consists of two components, a sample conditioning station and an analyzer unit. The conditioning station incorporates an incubator for sample equilibration and a humidifier unit for adjusting the humidity of the



FIG. 1—Block diagram of the AromaScanner electronic aroma detection device showing the basic operating components of the system.

reference air. The analyzer unit houses the sensor array and connections to the sampling port.

The AromaScanner detects the composition of an aroma using an array of 32 electrically conducting, organic polymer sensors that respond to different volatile (and semi-volatile) chemicals to yield a unique "fingerprint" for each vapor sample. An inking or masking process is used to put the polymer sensors on a single computer chip or board. The sensors are based on the polymers of aniline, pyrrole, and thiophene to which different functional groups have been added to produce unique sensing capabilities. The sensors respond to the steric, ionic, hydrophobic, and hydrophilic variations of a sample causing temporary changes in electrical resistance at the polymer surface. The kinetics of the reversible adsorption and desorption processes occur rapidly at room temperature once equilibrium has been achieved.

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 for the sensors. Next the volatiles that had accumulated in the headspace of the sealed pouch were pulled across the sensors until the sensor response reached equilibrium. For this study, a sampling time of 2 minutes was sufficient for this purpose. Any residual sample vapors were removed from the sensors during the wash step. A wash solution of 2% butanol (recommended by the manufacturer) was found to be effective for this purpose. In the final step, reference air was sampled again to ensure that the sensor response returned to their previous baseline readings. The raw data collected during acquisition is shown in the line graph in Fig. 2a. This figure shows the individual response of each sensor over time for each of the four steps in the method sequence.

Data Manipulation

After acquisition of the raw data, data manipulation software (supplied with the instrument) was used to develop databases containing patterns that are characteristic of the specific sample aromas. This was done by selecting the region of raw 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 then added to the database by averaging the sensor readings over the specified time interval to produce a fingerprint pattern or histogram, shown in Fig. 2b. Database entries can then be manipulated using two working modes: difference and superimpose to provide quick comparisons. The databases can also be mapped to provide a pictorial representation, or AromaMap, of pattern similarity or difference. The statistical technique used in the data mapping software is based on Sammon mapping (23).

The final stage of data processing involved the evaluation of an artificial neural network to classify aromas. The neural network software uses proprietary pattern recognition algorithms employing feed-forward fuzzy networks (24). Global classes are defined by the user to be representative of the samples being classified. The databases containing sets of sensor data patterns are called descriptor databases and are used by the neural network as sub-classifiers. These are the basic elements used in the pattern recognition process. The training process used by the software is supervised feedforward using a three-layer network and fuzzy back-propagation pattern recognition (25). The term feed-forward means that information flows in only one direction while the term fuzzy is indicativeof the addition of nodes in the output layer that represent an





FIG. 2—The line graph (a) shows the raw data output from the sensor array and illustrates the four step sequence used for data acquisition. The histogram (b) is an average of the sensor data over the time interval indicated by the cross-hairs shown in (a).



FIG. 3—Replicate fingerprint patterns showing normalized response versus sensor element number for six ignitable liquid 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).

unknown category. For this study, the neural network was trained using 4 global classifiers (control, diesel fuel, gasoline, and kerosene) and 3 sub-classifiers (neat, weak residue, and strong residue).

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 (26,27). 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 ignitable liquid 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 pure liquids are shown in Fig. 3. These plots, shown as line graphs rather than histograms, depict normalized response versus sensor element number. Although these patterns show some similar characteristics, the individual chemicals can be distinguished based on these fingerprint patterns as illustrated in the corresponding AromaMap, Fig. 4. An AromaMap is a multi-dimensional compression of the fingerprint 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 (23). Measurement of the Euclidian distance between patterns of two aromas can be used to provide a quantifiable indication of the difference between them. The larger the Euclidian distance, the more distinguishable are the aromas. As a general guideline, Euclidian distances <0.5 indicate two aromas are indistinguishable. The Euclidian distances between each of the neat ignitable liquids are shown in Table 1. The numbers in bold show the Euclidian distances between two analyses of the same sample which were slightly greater than 0.5 for most of the analytes. This most likely suggests a problem with run-to-run reproducibility or changes in sample concentration after successive analyses. The Euclidian distances between two different chemicals



FIG. 4—A multi-dimensional compression of the neat accelerant fingerprint data (shown in Fig. 3) into a 2-dimensional plot, or AromaMap, defining the magnitude of the sample aroma differences by distance and direction.

were generally much greater indicating the ability to distinguish these liquids. The exceptions were mineral spirits and kerosene which had the lowest Euclidian distance and most similar patterns and showed some overlap in the AromaMap (Fig. 4). Because sensor response can be affected by humidity and the intensity of the sensor response can be correlated with temperature, sample concentration, and equilibration time, it is believed that this problem may be overcome by adjusting the sampling conditions. Ultimately, the uniqueness of the fingerprint patterns can be optimized by choosing different regions of the data to assure the most distinct pattern has been selected.

Although the ability to distinguish different accelerants in the pure liquid form was just demonstrated, the aroma from pyrolysates may complicate the identification of the accelerants as residues in fire debris. To investigate this, accelerant residue samples from actual fire debris were obtained from a controlled burn of an abandoned house. The samples were obtained by spreading 1-2 L of gasoline, kerosene, and diesel fuel across separated 1-2 ft areas of carpeting within the living room area of the house. The fire was ignited and allowed to burn until the fire had spread throughout the living room area and had consumed each of the areas containing the ignitable liquid accelerants at which time it was then extinguished with water. Fire debris samples consisting of carpeting, carpet backing or padding, and wood flooring were collected from each of the areas where the liquids were known to have been poured. Confirmation that the samples contained the chemicals of interest was determined by trained Fire Investigation personnel using sense of smell. Further confirmation was provided by comparing the fingerprint patterns of these samples with those obtained from burnt carpet fragments fortified with small amounts of the liquids. Alternate techniques such as GC/FID or GC/MS would have been required to unequivocally confirm the presence of the accelerants in these samples. Although these lengths were not taken in this preliminary investigation, future studies would include a secondary method of confirmation.

Distinguishable fingerprint patterns were obtained for the three residues tested and the control fire debris sample as shown in Fig. 5. This figure shows the results for eight replicate analyses of each sample. The patterns for the residues were also found to be different from those of the neat liquids which can be seen in the clustering of these samples in the AromaMap, Fig. 6. This difference can be attributed to both the aroma from the pyrolyzed substrate material and the weathering of the flammable liquid. Run-to-run variation, identified by the loose clustering in the AromaMap and the reproducibility of the fingerprint patterns, was also observed especially for kerosene in both the neat and strong residue samples. This may be attributed to slight changes in the sample composition with equilibration time or inconsistent sampling conditions. Such factors as inconsistent sampling, variations in sample composition or residue concentration, and fire to fire consistency may be limiting factors for successful application of this technology.

Training of the artificial neural network was performed using the databases created for the neat ignitable liquids and "known" accelerant residues. The databases shown in the AromaMap, Fig. 6, were used to train the neural network for classifying the "unknown" fire debris samples collected from the controlled house fire. The neural network was set up using gasoline, kerosene, diesel fuel and control as the global classifiers. The subclass identifiers were either neat, weak or strong residue. Eight replicate analyses of each sample were used in the training set. The strong residue samples used in the training set were then re-analyzed seven times over a period of 1 to 15 days and the resulting data was used to



FIG. 5—Fingerprint patterns for the (a) control sample 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.

validate the neural network training set. These results can also be used to reflect the sample integrity with respect to loss of sample from the pouch, changes in sample humidity with time, and changes in aroma composition or concentration with equilibration time. The results for the validation of the neural network are shown in Table 2. The numbers given in the parentheses indicate the fit. The diesel fuel residue sample was classified with the correct global and subclass for all seven analyses. These results suggest that sample integrity and loss of sample from the pouch were negligible over the course of this study. The gasoline residue was classified with the correct subclass each time, but incorrectly identified with diesel fuel as the global class 6 out of seven times. It is unclear at this time why this result was obtained, however, it is believed that additional data manipulation or further training of the neural network may eliminate or minimize this problem. The kerosene residue was classified with the correct global and subclass four out of seven times. Only one analysis was misidentified as unknown for both the global and subclasses. 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 subclass. This is not surprising considering how closely the neat and strong residue samples for kerosene clustered in the AromaMap

Accelerant Gasoline Kerosene Diesel Fuel Mineral Spirits Lacq	uer 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.



FIG. 6—AromaMap of the "known" samples (neat ignitable liquids and accelerant residues) used to train the artificial neural network for classifying "unknown" fire debris.

shown in Fig. 6. When two patterns overlap, the neural network may have difficulty in making a distinction between them. Adjusting the sampling conditions or sample composition may help make these two samples more distinct.

After validation of the training set using the "known" strong residue samples, the neural network was evaluated by analyzing the "unknown" fire debris samples collected from the controlled house fire. Fire debris samples consisting of fragments of carpeting and related materials were collected in paint cans from each of the three areas where the ignitable liquids were known to have been poured. The paint cans were labeled as item 1, item 3, and item 5 where each item should have contained one of the three different accelerants used in igniting the fire. Prior to analysis, 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 neural network. Eight replicate analyses were performed for each sample and the results were predominantly identified by the neural network as diesel fuel for all six items. It was noted that four of the six items had excessively high humidities ($\geq 12.0 \text{ g/m}^3$) during sample acquisition that were outside the range of the reference samples used to train the neural network ($7 \sim 10.0 \text{ g/m}^3$). Only the two samples corresponding to item 3 had sample humidities in the correct range. This suggests that fingerprint patterns for these two samples were not effected by the sensor response to water. Confirmation of this can be seen by comparing the fingerprint patterns for these samples with that of the "known" diesel fuel residue, Fig. 7. Both items 3a and 3b were classified with the correct global class, diesel fuel, with fits

TABLE 2—Validation of the neural network using the strong residue samples.

Analysis	Gasoline Global	Sub-class	Kerosene Global	Sub-class	Diesel fuel Global	Sub-class	
1	diesel fuel	gas.res.str.	kerosene (99.9)	ker.neat	diesel fuel	dies.res.str.	
2	gasoline (93.5)	gas.res.str. (96.5)	kerosene (82.3)	(75.5) ker.res.str. (77.1)	diesel fuel (99.9)	dies.res.str. (98.7)	
3	diesel fuel	gas.res.str.	kerosene	ker.res.str.	diesel fuel	dies.res.str.	
	(93.6)	(95.5)	(91.0)	(86.9)	(99.9)	(99.0)	
4	diesel fuel	gas.res.str.	kerosene	ker. neat	diesel fuel	dies.res.str.	
	(99.4)	(97.4)	(99.9)	(91.6)	(100.0)	(99.1)	
5	diesel fuel	gas.res.str.	unknown	unknown	diesel fuel	dies.res.str.	
	(99.4)	(85.6)	(100.0)	(100.0)	(99.9)	(94.8)	
6	diesel fuel	gas.res.str.	kerosene	ker.res.str.	diesel fuel	dies.res.str.	
	(99.0)	(87.9)	(98.9)	(86.9)	(99.9)	(94.5)	
7	diesel fuel	gas.res.str.	kerosene	ker.res.str.	diesel fuel	dies.res.str.	
	(96.0)	(92.7)	(96.7)	(91.1)	(99.9)	(82.5)	

*Numbers in () indicate fit.



FIG. 7—Fingerprint patterns for the fire debris samples corresponding to item 3. Both samples 3a (b) and 3b (c) were identified by the neural network as diesel fuel residue (a).

 \geq 91.0 for each of the eight replicate analyses. The subclass identified for these samples varied between weak and strong diesel fuel residue with fits ranging from 70.0 to 99.0.

For items 1 and 5, it is speculated that the excessively high sample humidities interfered with the sensor response because all 32 sensors will respond moderately to water. The higher humidities for the "unknown" samples relative to the "known" may be attributed to the different storage containers used. The "known" fire debris samples were collected in pouches and analyzed almost immediately, while the "unknown" fire debris samples were collected in paint cans where they were stored prior to analysis. This difference has made apparent the fact that variations in the water content between samples may effect the accuracy of neural network classification. This again alludes to the fact that fire to fire consistency may be the limiting factor for this technology. For example, the effects of weathering can be varied and unpredictable and may also have contributed to these results. Because of these effects, a means of decreasing the sample humidities was investigated to obtain a more accurate sensor response and pattern.

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 (28). After sitting overnight, the Drierite[®] was removed and the samples were re-analyzed. Re-analysis of these samples showed no decrease in sample humidity and no change in neural network classification indicating 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. The results for item 1b are shown in Fig. 8. The fingerprint patterns for item 1b (8c) and the Drierite® used to sample item 1b (8d) are compared to those for the "known" gasoline residue (8a) and neat gasoline (8b). The sorbent sample pattern compares remarkable well with the neat gasoline sample and neural network global-class fits of 95.3 and 97.0 were obtained for this sample. The subclass identifier for the sorbent sampled item 1b was neat gasoline with fits of 94.3 and 99.2. Even with the use of the sorbent, item 1a was still occasionally mis-identified by the neural network as either unknown or kerosene. Correct global class fits for item 1a were 86.1 for duplicate analyses with subclass identifiers being either unknown or neat diesel fuel. The problems associated with the neural network classification 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. These results demonstrate the need to control sampling conditions and to minimize variations in sample composition to achieve consistent results and proper neural network classification. Because the sorbent results were so promising, future work will include such reference samples in the training set.

Because item 5 was classified as a weak kerosene residue for two of the eight original analyses, it was speculated that other variables besides humidity may have contributed to the misclassifications. 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). The Drierite[®] sorbent was



FIG. 8—Fingerprint patterns for gasoline as the (a) accelerant residue, (b) neat ignitable liquid, (c) item 1b, and (d) the Drierite® used to concentrate the vapors from item 1b.

also used to concentrate the accelerant vapors from samples containing item 5. After analysis of the sorbent, both items 5a and 5b were correctly identified as kerosene. Global class fits for triplicate analyses of these samples were \geq 95.8. The subclass was always identified as a weak kerosene residue with fits \geq 96.0. These results illustrate the potential advantages of sorbent sampling to concentrate accelerant vapors prior to aroma detection.

Conclusions

The use of aroma detection technology for detecting ignitable liquid accelerants in fire debris was shown to be feasible. It was determined that the variables affecting a change in sensor response, humidity, temperature, and equilibration time, need to be precisely controlled to achieve consistent results. For reference samples, this can be accomplished by controlling the temperature and humidity of the reference air and equilibrating the sample under these conditions 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 composition and concentration were shown to influence the sensor response. Neural network classifications were often affected because reference and fire debris sampling conditions and sample composition were inconsistent. Sorbent sampling prior to aroma detection was demonstrated to reduce these problems and to improve neural network classification. 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, 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 addressing some of these issues.

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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