Raymond O. Keto,[1] *B.S., M.F.S.*

Comparison of Smokeless Powders by Pyrolysis Capillary Gas Chromatography and Pattern Recognition

ABSTRACT: Four smokeless powder propellants from each of three domestic manufacturers were analyzed by pyrolysis capillary gas chromatography. Pyrograms were compared to see if this was a viable technique for the identification of a questioned smokeless powder. Comparisons were made between particles from the same manufacturer's product and lot, between different lots of the same manufacturer's product, and between different manufacturers' products. The differences between the pyrograms were less than anticipated, and some of the manufacturer's products could not be differentiated from others. Correlation values were computed to quantify the degree to which each pyrogram matched each of the others. The correlation values for within-product comparisons averaged 97.1 out of a possible 100, whereas those for between-product comparisons averaged 80.0. The range of correlation values for between-product comparisons overlapped the range of correlation values for within-product comparisons. This limited the conclusion that could be drawn regarding the origin of a smokeless powder in question.

KEYWORDS: forensic science, explosives, chromatographic analysis, propellants, smokeless powder, gas, capillary, pyrolysis, nitrocellulose, pattern recognition, correlation factors

Smokeless powder is a propellant formulated and manufactured for use in firearms. It is readily available in 1-lb (0.45-kg) canisters at sporting goods stores and is used by firearms enthusiasts in reloading cartridge casings and shot shells. Representative particles of smokeless powder manufactured for small arms use are shown in Fig. 1. The ingredients commonly incorporated into smokeless powder are listed in Table 1.

Smokeless powder has also found widespread illegitimate use in the fabrication of improvised explosive devices. The most common of these devices is the pipe bomb, which, when properly constructed, can be as deadly as dynamite. When a pipe bomb explodes, unburned particles of smokeless powder may be scattered about in the vicinity of the blast seat. These particles can often be recovered by investigators and forwarded to the crime laboratory for identification.

The identification of smokeless powder from a bomb scene begins with the separation of intact suspect particles from the debris and their characterization by size, shape, color, texture, and flammability. The identification of nitrocellulose and nitroglycerine (in double-base powders) by chemical or instrumental techniques is all that is necessary to confirm the
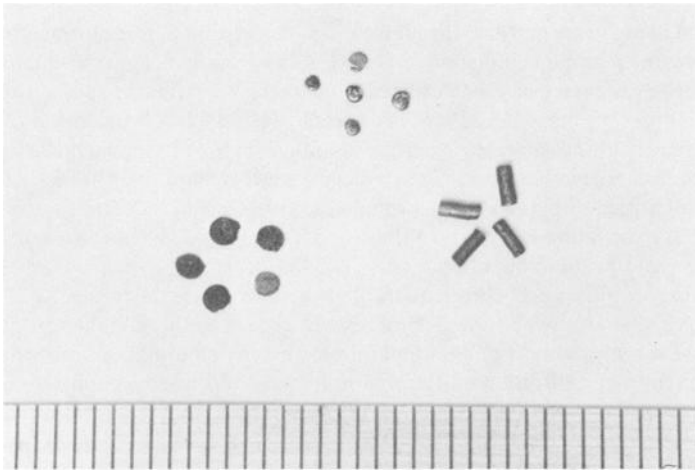
FIG. 1—*Types of smokeless powder studied:* (left) *disk/wafer (Hercules & DuPont Hi-Skor);* (right) *tube/cylinder (DuPont IMR); and* (top) *flattened ball (Olin/Winchester-Western) (scale in millimetres).*

TABLE 1—*Typical ingredients used in smokeless powders.*

BASE:	**BURNING MODIFIERS** (cont.)
Single—nitrocellulose	DNT
Double—nitrocellulose and	Ethyl centralite
nitroglycerine	Diphenyl phthalate
	Starch
ADDITIONAL EXPLOSIVES/OXIDIZERS:	Agar
Nitroguanidine	Vinsol
TNT	
DNT	**PLASTICIZERS:**
KNO_3	Diethyl phthalate
$BaNO_3$	Dibutyl phthalate
	Dioctyl phthalate
STABILIZERS:	Triacetin (glycerol triacetate)
Diphenylamine	
Ethyl centralite (diethyldiphenyl urea)	**COATING:**
$NaHCO_3$	Graphite
Basic lead carbonate	Carbon black
Petrolatum	
	RESIDUAL SOLVENTS:
BURNING MODIFIERS:	Ethanol
K_2SO_4	Acetone
Na_2SO_4	Diethyl ether
SnO_2	Ethyl acetate
Tin	Benzene
	H_2O

presence of smokeless powder. However, these examinations cannot determine the source of the powder in question, such as a particular canister or production lot. More definitive techniques are desired for the source identification and comparison of smokeless powder samples.

The source identification of smokeless powders has been approached by several researchers using various analytical techniques. Gas chromatography/mass spectrometry (GC/MS)

has been used to associate powders through a quasi-fingerprint pattern formed by a composite mass spectrum of major component peaks [1]. A combination of gas chromatography and proton magnetic resonance has been utilized to characterize various manufacturers' product types [2]. High-performance liquid chromatography (HPLC) has been shown to be a viable means of separating and characterizing the soluble components of smokeless powder [3], and some researchers have claimed that smokeless powders and their partially burned residues can be identified by pyrolysis gas chromatography [4]. None of these papers describe an appropriate statistical analysis to show that the given method yields consistent results and can be relied on to make an identification.

In this study, capillary gas chromatography was investigated as a means of comparing single particles of smokeless powder. Pyrolysis was chosen as the sample introduction technique because it required no sample preparation, thereby eliminating problems associated with the extraction and filtration of liquid samples. In addition, the capillary column chromatography of the smokeless powder pyrolyzate was found to yield a good number of individual chromatographic peaks, providing the potential for a high degree of discrimination between similar powders. Samples were limited to single particles to see if valid comparisons could be made on the smallest unit of powder, thereby conserving evidence.

Equipment and Materials

The pyrolysis and gas chromatographic separation parameters are listed in Table 2. The pyrolysis unit was used with the quartz tube pyroprobe inserted directly into the chromatograph injection port. This required that the injection port liner be reduced in length by several centimetres to accommodate the probe.

Data (peak retention time and area) were collected with a Perkin-Elmer Chromatographics Intelligent Terminal Model 3600 data station. Pyrograms were compared by inserting peak area data into a program written in BASIC and run on a Digital Equipment LSC-1103 computer.

TABLE 2—*Instrumental parameters.*

	GAS CHROMATOGRAPHY	
Instrument	Perkin-Elmer Sigma 3B	
Column	J & W Scientific DB-WAX	
	(Polar bonded phase)	
	30-m capillary column	
	0.25-μm phase thickness	
Carrier gas	Helium, 138 kPa (20 psi)	
	Flow rate = approximately 2 mL/min	
Injector	Modified for pyrolysis and capillary column	
	Temperature: 140°C	
Detector	Flame ionization	
	Temperature: 250°C	
Oven	Initial temperature	40°C
	Initial hold	1 min
	Program	25°C/min
	Final temperature	240°C
	Final hold	5 min
	ANALYTICAL PYROLYSIS	
Instrument	Chemical Data Systems pyroprobe Model 120	
Element	Coil	
Carrier	Quartz tube	
Program	Temperature	400°C
	Duration	5 s
	Ramp	off

The samples analyzed consisted of reloader powders that had been purchased at retail outlets in 1-lb (0.45-kg) canisters. Four products from three manufacturers were chosen: Du-Pont (IMR 3031, IMR 4064, IMR 4320, and Hi-Skor 700X powders), Hercules (Red Dot, Blue Dot, Green Dot, and Bullseye powders), and Olin/Winchester Western (452AA, 540, 630, and 748 powders).

Experimental Procedure

Three particles of smokeless powder were analyzed individually as taken at random from each canister. To avoid the introduction of additional variables, colored marker wafers (such as those in the DuPont Hi-Skor 700X and Hercules Red Dot, Blue Dot, and Green Dot products) and partial particles were not chosen. Higher pyrolysis temperatures and longer durations than those given in Table 2 were found to have minimal effect (if any) on the resulting pyrogram. This was due to the combustion of the smokeless powder, since it carries its own oxygen and can burn in an inert atmosphere. The temperature attained by the burning powder particle is much higher than that of a pyroprobe operating at normal pyrolysis temperatures. The pyroprobe merely initiates the combustion and has little control over the final temperature attained.

The relatively low injection port temperature was found to be necessary to prevent the spontaneous combustion of the sample upon insertion of the pyroprobe. The initiation temperature of smokeless powder varies from product to product and has been reported to be as low as 165°C (329°F) [5]. The injection port temperature was set at 25° below this temperature to avoid any possibility of premature ignition. Because of the volatization of some smokeless powder components (such as residual solvents and plasticizers) in the injection port, a constant delay interval of 20 s was taken between the insertion of the sample probe and pyrolysis to ensure reproducible sampling.

In the preliminary phase of this study, a comparison was made between a relatively nonpolar capillary column (J & W DB-5) and the polar DB-wax. The DB-5 column did not adequately retain the early eluting components and gave poor resolution to later eluting peaks (Fig. 2). The DB-wax column gave much better retention to the early components and near baseline resolution to all of the peaks of interest. No other columns were tested. A split injection ratio of about 20 to 1 was used for most of the separations. A ratio of about 8 to 1 was found to be useful when pyrolyzing the very small particle powders.

The pyrograms of the three individual particles from each manufacturer's product were compared among each other and with the pyrograms of the particles from each of the other products.
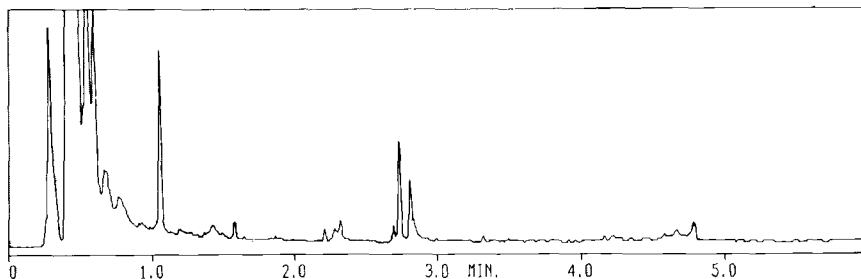

FIG. 2—*Pyrogram of a typical smokeless powder run on a nonpolar capillary column (J & W Scientific DB-5).*

Results

Typical pyrograms of three different manufacturer's products are shown in Fig. 3. The first two peaks eluting before Peak 1 were not included for comparison purposes because of their lack of retention and poor chromatographic characteristics. These peaks may contain volatile components that evaporated from the sample in the heated injection port before pyrolysis or gaseous products of pyrolysis (such as methane, ethane, and so forth) or both.

In comparing the remaining peaks in these pyrograms, it was anticipated that major differences would be seen between them based on the results of previous researchers in the field [4]. However, this was not the case. Preliminary visual comparisons did not reveal any striking differences between the pyrograms. Closer inspection revealed variations in relative peak intensities that appeared to be greater between the products than they were among the particles within each product. The magnitude of the between-sample variation can be seen in the relative heights of Peaks 5 and 6 and Peaks 9, 10, and 11 in Fig. 3. All of the pyrograms obtained on the twelve products studied resembled to a greater or lesser extent the three pyrograms shown.
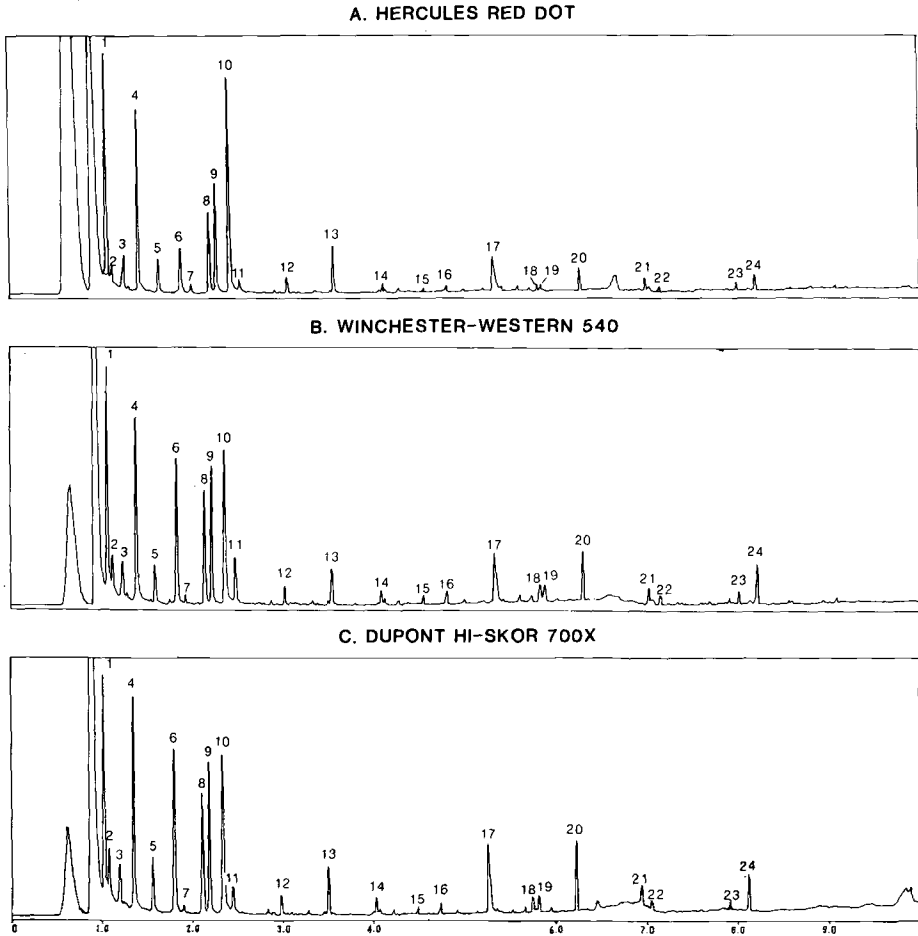

FIG. 3—*Pyrograms of single smokeless powder particles from three different manufacturer's products (time scale in minutes).*

Because of the high degree of similarity between the pyrograms, correlation values were computed to rate each pyrogram as to its similarity (100 indicates perfect overlap) or dissimilarity (0 indicates no peaks in common) to each of the other 35 pyrograms generated.

Data Manipulation

Peak numbers were assigned to 24 prominent peaks in a pyrogram. Corresponding numbers were assigned to peaks in all of the other pyrograms by overlaying them on this "master" pyrogram over a light box. In this way, slight shifts caused by day-to-day variations in the chromatography could be easily recognized. The areas for the numbered peaks were then obtained from the data station print-out.

A computer program was written in BASIC to determine the degree to which the 24 peaks in two prospective pyrograms agree. The correlation value, C, is defined as

$$C = 100 \left[\frac{[(A_1 B_1) + (A_2 B_2) + \ldots + (A_{24} B_{24})]^2}{(A_1^2 + A_2^2 + \ldots + A_{24}^2)(B_1^2 + B_2^2 + \ldots + B_{24}^2)} \right]$$

where $A_1, A_2, \ldots$, and A_{24} equal areas for Peaks 1 through 24 for Pyrogram A and $B_1, B_2, \ldots$, and B_{24} equal areas for Peaks 1 through 24 for Pyrogram B. The computed value within the large brackets in this expression is the square of the cosine of the angle between the two pyrograms when plotted as vectors in 24-dimensional space, with each dimension representing the area of one chromatographic peak. (The vectors are defined by the origin and points determined by the peak areas in each respective pyrogram.) This value is multiplied by 100 to give the correlation value.

This type of correlation analysis is similar to that used in other pattern recognition techniques [6–8] and cluster analysis [8,9]. The cosine function was used instead of the Euclidean distance between the points because the interest here was in generating a dimensionless number rather than a visual representation. Since the cosine function is the trigonometric ratio of the two vectors, the calculation is "self-normalizing" and independent of vector length (sample size). Correlation values based on the cosine function are used routinely for spectral library searches in the field of mass spectrometry [10], and are also applicable to chromatographic data [8].

Table 3 lists the results of the comparison of pyrograms for the twelve powders analyzed. The top number in each column is the average correlation value for the three particles within each powder sample. These values were obtained by computing the correlations of Particle A versus Particle B, Particle B versus Particle C, and Particle C versus Particle A, and averaging them. These within-sample averages range from 92.9 to 99.2, with an overall average of 97.1 ± 1.9 (standard deviation). Assuming a normal distribution for these averages (a questionable assumption at this point), it can be shown with 99% confidence that 75% of all within-sample comparisons averages will have a correlation value of 94.8 or higher.

The other 66 values in Table 3 are averages of nine correlation values calculated for each between-sample comparison (three particles of one powder versus three particles of another). These averages range from 42.4 to 98.3, with an overall average of 80.0 ± 11.6. Again, assuming a normal distribution for this data, it can be shown with 99% confidence that 75% of all between-sample comparison averages will have a correlation value of 92.7 or lower. Thus, using normal distribution statistics, it appears that the overlap point between the two populations is between 92.7 and 94.8.

Histograms for both sets of data are shown in Figs. 4 and 5. It appears that neither of these distributions is normal and that statistical calculations based on normal distributions may not be valid in this situation. A look at the data in Table 3 shows that five of the 66 between-sample values (7.6%) are 92.9 or greater and overlap the range of values for the within-sample comparisons.

TABLE 3—*Correlation values calculated for smokeless powder comparisons.*

|	RED DOT	BLUE DOT	GREEN DOT	BULLS-EYE	WW 452AA	WW 540	WW 630	WW 748	IMR 4064	IMR 4320	IMR 3031	HS 700X
RED DOT	98.8											
BLUE DOT	78.4	95.1										
GREEN DOT	90.2	91.4	97.1									
BULLSEYE	74.6	42.4	63.7	97.4								
WW 452AA	86.7	77.4	88.6	70.5	98.9							
WW 540	82.1	76.7	85.6	58.8	91.6	92.9						
WW 630	82.3	57.9	77.4	81.7	80.5	81.2	95.6					
WW 748	84.0	76.4	86.3	63.1	93.9	93.9	80.1	99.2				
IMR 4064	87.1	87.7	93.6	61.2	92.9	92.1	77.4	92.6	97.8			
IMR 4320	74.8	74.3	79.1	51.9	84.0	81.7	66.4	84.2	82.1	99.1		
IMR 3031	74.6	76.9	80.1	50.1	83.8	81.1	64.0	82.9	82.9	98.3	97.2	
HS 700X	89.5	79.8	92.7	69.9	92.0	91.4	88.2	91.3	92.6	78.4	77.9	96.1
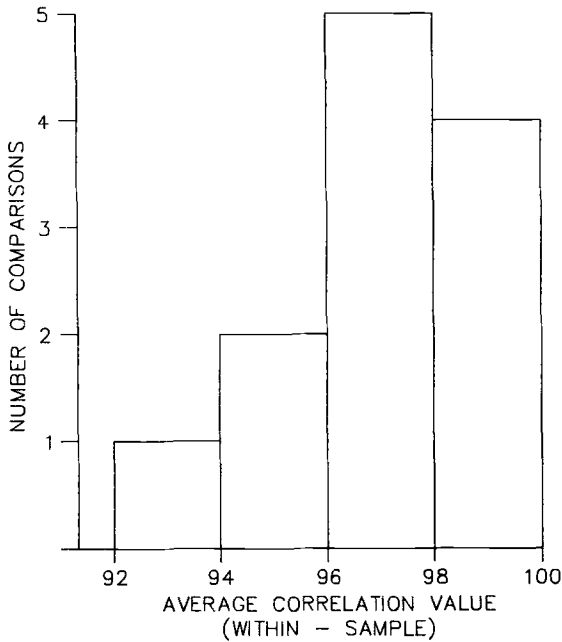
FIG. 4—*Histogram of average correlation values for within-sample comparisons.*

In either case (normal or skewed distributions) there is a substantial overlap of values between samples that are known to match and samples that are known to be from different sources. As a result, it is not possible to establish a particular correlation value above which an unknown comparison could be unequivocably identified as a match.

The method does have limited value, however. The higher the correlation value, the greater the probability that a given comparison is of two particles that originated from the
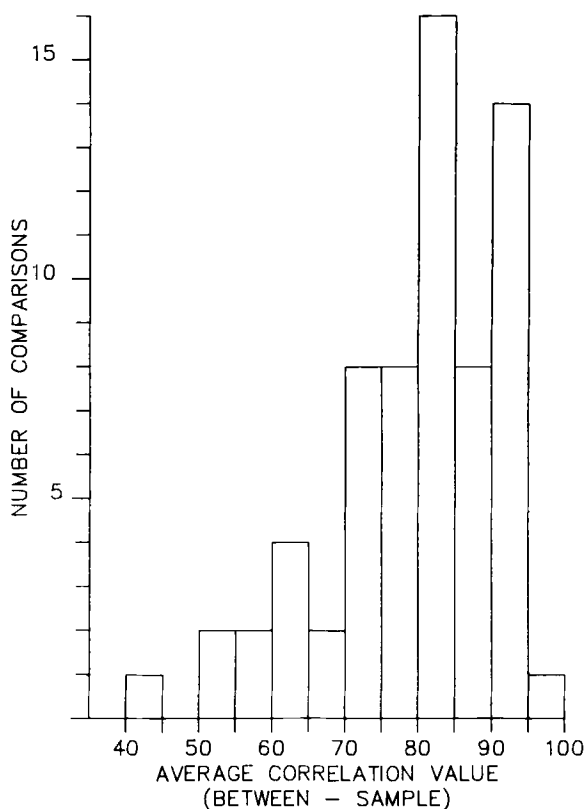
FIG. 5—*Histogram of average correlation values for between-sample comparisons.*

same manufacturer's product line. For example, if we require that the correlation average between 2 samples be 95 or better before we call them a match, the data shows that the probability of committing a Type I error [11] (failing to find a match where one exists) is about 1 chance in 12, and that that of committing a Type II error (finding a match where none exists) is about 1 chance in 66.

Lot Comparisons

Lot-to-lot variations were examined for Hercules Bullseye and DuPont Hi-Skor 700X smokeless powders. Six individual particles of each of two lots were analyzed for each product, giving a total of fifteen within-lot comparisons and thirty-six between-lot comparisons. The resulting correlation value averages are given in Table 4. The within-lot correlation values are, for all forensic purposes, indistinguishable from the between-lot values. This is as expected, given the low degree of product distinguishability found previously for the between-sample comparisons.

Conclusions

Relatively minor differences exist between the pyrograms of smokeless powder from different manufacturers. Based on the data generated in this study, pyrolysis capillary gas chromatography has only limited value for the source identification of smokeless powders.

TABLE 4—*Lot comparisons.*

	A. Hercules Bullseye			B. DuPont Hi-Skor 700X	
	Lot I	Lot II		Lot I	Lot II
Lot I	97.3[a]	...	Lot I	99.4[a]	...
	(±2.2)	...		(±0.5)	...
Lot II	96.7[b]	97.8[a]	Lot II	98.6[b]	98.7[a]
	(±2.9)	(±1.9)		(±.8)	(±1.5)

[a] n = 15 pairs.
[b] n = 36 pairs.

Correlation values for replicate pyrograms of smokeless powder particles from the same source averaged 97.1 (out of a possible 100) whereas correlation values for pyrograms of particles from different sources averaged 80.0. The range of correlation values for the same-source comparisons overlapped the range of correlation values for the different-source comparisons.

No significant differences were found between the pyrograms of smokeless powder particles from different lots of the same manufacturer's product line.

References

[1] Martz, R. M. and Lasswell, L. D., III, "Smokeless Powder Identification," *Proceedings of the International Symposium on the Analysis and Detection of Explosives,* Federal Bureau of Investigation, Washington, DC, 1984, pp. 245–254.

[2] Meyers, R. E. and Meyers, J. A., "Instrumental Techniques Utilized in the Identification of Smokeless Powders," *Proceedings of the International Symposium on the Analysis and Detection of Explosives,* Federal Bureau of Investigation, Washington, DC, 1984, pp. 93–106.

[3] Bender, E. C., "Analysis of Smokeless Powders Using UV/TEA Detection," *Proceedings of the International Symposium on the Analysis and Detection of Explosives,* Federal Bureau of Investigation, Washington, DC, 1984, pp. 309–320.

[4] Newlon, N. A. and Booker, J. L., "The Identification of Smokeless Powders and Their Residues by Pyrolysis Gas Chromatography," *Journal of Forensic Sciences,* Vol. 24, No. 1, Jan. 1979, pp. 87–91.

[5] DeHaan, J. D., "Quantitative Differential Thermal Analysis of Nitrocellulose Propellants," *Journal of Forensic Sciences,* Vol. 20, No. 2, April 1975, pp. 243–253.

[6] Miller, J. C. and Miller, J. N., *Statistics for Analytical Chemistry,* Ellis Horwood Limited, Chichester, U.K., 1984.

[7] Andrews, H. C., *Introduction to Mathematical Techniques in Pattern Recognition,* Wiley, New York, 1972.

[8] Jurs, P. C., "Chemical Applications of Pattern Recognition and Cluster Analysis," *Statistics,* R. F. Hirsch, Ed., The Franklin Institute Press, Philadelphia, 1978.

[9] Morgan, S. L., Walla, M. D., and Rogers, J. C., "Measuring and Displaying Chromatographic Similarity Using Cluster Analysis," *Chromatography,* Vol. 2, No. 6, July 1987, pp. 12–20.

[10] Finnigan MAT 1000 Series GC/MS System Operator's Manual No. 10000-90098, Revision A, Finnigan Corp., Sunnyvale, CA, 1981, pp. 2/25–2/31.

[11] Burlington, R. S. and May, D. C., *Probability and Statistics,* McGraw-Hill, Handbook Publishers, Inc., Sandusky, OH, 1953, p. 222.

Address requests for reprints or additional information to
Raymond O. Keto
Forensic Chemist
Bureau of Alcohol, Tobacco, and Firearms
1401 Research Blvd.
Rockville, MD 20850