

Standard Guide for Using Pyrolysis Gas Chromatography and Pyrolysis Gas Chromatography-Mass Spectrometry in Forensic Paint Examinations

Scientific Working Group on Materials Analysis (SWGMAAT)

Introduction

Various analytical techniques are available for the forensic analysis of paint. The evidentiary samples typically received by forensic laboratories may be relatively small and therefore require techniques that can provide the most information with as little sample consumption as possible. Although destructive in nature, pyrolysis gas-chromatography (Py-GC) and pyrolysis gas-chromatography/mass spectrometry (Py-GC/MS) can provide a large amount of organic chemical information from such samples. This information can be used to augment that obtained from other analytical techniques such as Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDS).

1.0 SCOPE

1.1 This document serves as a guide to assist individuals and laboratories in the utilization of Py-GC and Py-GC/MS in the forensic examination of paint. It will address the selection, application and evaluation of Py-GC and Py-GC/MS as methods for the identification and comparison of the organic components of paints.

1.2 This guideline does not purport to address any safety concerns associated with its use. It is the responsibility of the user of this document to establish appropriate health and safety practices and to determine the applicability of regulatory limitations prior to use.

2.0 REFERENCED DOCUMENTS

2.1 ASTM International Standards

D16-11 Terminology for Paint Related Coatings, Materials and Applications

E 1459-92(2005) Standard Guide for Physical Evidence Labeling and Related Documentation

E 1492-11 Standard Practice for Receiving, Documenting, Storing and Retrieving Evidence in a Forensic Science Laboratory

E1610-02(2008) Standard Guide for Forensic Paint Analysis and Comparison

2.2 Scientific Working Group for Materials Analysis

SWGMAAT Trace Evidence Quality Assurance Guidelines (January 2000). Available:

www.swgmat.org/Trace%20Evidence%20Quality.pdf

SWGMAAT Trace Recovery Guidelines (October 1999). Available:

www.swgmat.org/Trace%20Evidence%20Recovery%20Guidelines.pdf

SWGMAAT Forensic Paint Analysis and Comparison Guidelines. Available:

www.swgmat.org/Forensic%20Paint%20Analysis%20and%20Comparison%20Guidelines.pdf

3.0 TERMINOLOGY

CAPILLARY COLUMN A long, narrow, wall coated, open tubular column used for capillary gas chromatography.

CARRIER GAS Mobile gas phase that flows through the column carrying the analyte.

CLASSIFICATION Separating samples into groups based on their properties or characteristics.

CHROMATOGRAM A presentation of data from a chromatographic system represented as a plot of the detector signal intensity vs. time.

CURIE POINT The temperature at which a ferromagnetic metal loses its ferromagnetic properties.

FLAME IONIZATION DETECTOR (FID) A detector that measures the concentration of organic species in a gas stream.

GAS CHROMATOGRAPHY (GC) An analytical separation technique that uses a gas (mobile phase) such as helium, nitrogen, or hydrogen to carry a mixture of analytes through a column that is either packed or coated with a stationary medium (stationary phase). In this technique separation occurs through differential interaction of analytes with the stationary phase.

GAS FLOW RATE The rate at which the carrier gas flows through the column.

GC TEMPERATURE PROGRAM An operator specified program that changes the temperature of the column oven over an analytical run through a computer interface.

INTERFACE TEMPERATURE The temperature of the heated zone between the pyrolysis unit and the GC.

MASS SPECTROMETRY (MS) An analytical technique that measures the mass-to-charge ratio (m/z) of gaseous ions.

MOBILE PHASE The carrier gas in a gas chromatographic system, which is inert to the sample (and moves through the chromatographic column, transporting the sample from inlet to the detector outlet).

MONOMER A repeating structural unit within a polymer.

PEAK RESOLUTION The ability to separate peaks.

POLYMER A high molecular weight compound consisting of one or more types of repeating units (monomers); it can be natural or synthetic.

PYROGRAM A chromatogram obtained from the pyrolysis products of a material.

PYROLYSIS The thermal fragmentation of a substance in an inert atmosphere.

PYROLYSIS TEMPERATURE The temperature at which the pyrolysis of the sample is performed. It can be a set temperature or a ramped temperature program depending upon the pyrolysis system.

PYROLYZATE The product of the pyrolysis process.

RETENTION TIME The time required for the elution of a component in a chromatographic system.

SPLIT RATIO The distribution of the carrier gas and injected sample between waste and the column.

STATIONARY PHASE The coating of the walls of a fused silica column. It is the phase that does not move in a chromatographic system.

TEMPERATURE PROGRAM The program set up through a computer interface by the operator controlling the temperature of the chromatographic oven.

TOTAL ION CHROMATOGRAM (TIC) The resulting display of the separated mixture after the mass spectrometer detects and identifies the components of the mixture.

TRACEABLE REFERENCE STANDARD A sample acquired or prepared with documented origin that has known properties for the purpose of calibrating equipment and/or for use as a control.

TRANSFER LINE The connection between the pyrolysis unit and the GC injection port, as well as between the GC and the MS.

4.0 SUMMARY OF PRACTICE

4.1 This guide outlines the application of qualitative and semi-quantitative Py-GC and Py-GC/MS in forensic paint analysis as described in E1610. It describes the pyrolysis of small samples, interpretation and comparison of pyrograms, and identification of the binder systems in paint. The analytical system consists of at least two distinct components: 1) the pyrolysis unit where sample pyrolysis occurs, and 2) the gas chromatograph where separation and detection of the pyrolyzate components occur. In instances where a mass spectrometer is utilized as a detector, it can be considered as a third distinct part of the analytical system. The use of a mass spectrometer assists in the identification of selected pyrolyzates.

4.2 Paint samples are complex mixtures of organic and inorganic components. Pyrolysis techniques are suitable for the analysis of the organic content. It should be noted that the inorganic content of the samples will remain behind in the sample holder after pyrolysis.

4.3 The primary organic constituent of any paint is the binder or resin. In addition to the binder, various other organic components may be present, including but not limited to pigments, plasticizers, and various additives, all of which may appear in the pyrogram and may have comparative value. As these techniques are destructive the amount of sample available must be taken into consideration. Analysis of individual paint layers is encouraged whenever practicable.

4.4 BASIC PRINCIPLES

4.4.1 Pyrolysis is the thermal fragmentation of a substance in an inert atmosphere. This process reduces larger molecules into smaller molecules through the breaking of bonds via the application of thermal energy. Analytical pyrolysis provides chemical information on various materials and enables the analysis of materials that cannot otherwise be introduced into a chromatographic system in liquid form. By operating in an inert atmosphere and strictly controlling temperature and the time of heating, macromolecular materials can be reduced to smaller molecules in a reproducible fashion. When analyzed using a separation technique such as gas chromatography, the smaller molecules produced through the action of pyrolysis will form a pattern of separated fragments carrying information about the original molecule. This procedure makes it possible to obtain structural information about high molecular weight compounds.

4.4.2 There are three primary mechanisms by which fragmentation can occur: 1) random scission, 2) monomer reversion, and 3) side group scission.

4.4.2.1 Random scission is a free radical mechanism that results in random breaks in a polymer chain. The breaks typically occur between carbon-carbon bonds on the polymer chain that have similar bond strengths. The resulting fragments have a terminal unsaturation and a range of lengths. A good example of a pyrogram produced through random scission is that of polyethylene.

4.4.2.2 Monomer reversion involves the unzipping of a polymer chain into its constituent monomers. This occurs when the bonds between monomers are the weakest links in the polymer chain. A good example of monomer reversion can be found in the pyrogram of polystyrene where the largest peak is styrene.

4.4.2.3 Side group scission occurs when side groups on a polymer chain in close proximity to one another form stable bonds with one another and are released from the polymer chain. The resulting products typically contain unsaturated bonds and may form aromatic products as in the case of polyvinyl chloride (PVC).

4.4.3 It should be noted that polymer compositions can be very complex and a combination of the above listed mechanisms commonly occur during the pyrolysis process. Examples and a thorough discussion of these mechanisms can be found in Wampler (2007).

4.4.4 The pyrograms that are produced from different polymer compositions form characteristic patterns that can be used for both identification of polymer type and comparisons between known and unknown samples.

4.5 INSTRUMENTATION

4.5.1 Pyrolysis Systems

4.5.1.1 Three different types of instrumentation are available for performing analytical pyrolysis: 1) resistively heated pyrolyzers, 2) Curie point pyrolyzers and 3) furnace pyrolyzers, all of which have advantages and disadvantages.

4.5.1.2 The most common form of pyrolysis used in the forensic laboratory is resistively heated pyrolysis. In this technique, the sample is placed either on a ribbon filament or in a quartz tube or boat that is inserted into a coiled filament. When a current is passed through the filament, resistance of the metal results in rapid heating. Transfer of heat from the filament results in pyrolysis of the sample. Temperature ramping is possible with this technique and the desired temperature can be selected by simply controlling the current. It should be noted that the coil set temperature and the amount of heat that actually reaches the sample may differ.

4.5.1.3 With inductively heated or Curie point pyrolysis, the sample is either coated on or placed in a ferromagnetic wire or foil. A radio frequency (Rf) electric current is introduced into a coil surrounding the wire or foil sample retainer. As the current passes through the coil, an electromagnetic field is generated causing the wire or foil to rapidly reach a maximum temperature (Curie point temperature) that pyrolyzes the sample. The type of wire or foil that is used will determine the maximum temperature that will be reached. This type of analysis results in temperatures that can be strictly controlled in a highly reproducible fashion. Different alloy compositions are available for a wide range of temperatures. Temperature ramping is not an option with this technique.

4.5.1.4 Furnace pyrolyzers use a quartz crucible to introduce the sample into the heated analytical chamber (furnace). The furnace is typically run isothermally (held at a single temperature). Furnace pyrolyzers are relatively inexpensive and easy to use. However, there is usually a large reaction space that can result in secondary fragmentation taking place and the relatively long equilibration times preclude the use of temperature ramping.

4.5.2 Gas Chromatography

4.5.2.1 The typical gas chromatograph contains an inlet for sample introduction, a temperature controlled oven, an analytical column(s), and a detector(s). Some systems also include a pyrolysis interface.

4.5.2.2 The inlet conditions must be suitable for the samples that are being introduced into the instrument. The inlet temperature must be high enough to prevent condensation of most pyrolysis fragments but not so high that secondary reactions and column degradation occur. The inlet temperature should not exceed the highest temperature of the oven in order to reduce the possibility of sample carryover. Typical inlet temperatures range from 200 to 300°C. The split ratio should be suitable for the sample sizes that are being analyzed. In general, the split ratio should be set so that the column and detector are not saturated by sample. A poorly chosen split ratio can result in poor chromatographic separations and saturated peaks in the chromatogram. Typical split ratios range from 20:1 to 100:1.

4.5.2.3 The choice of oven parameters is critical for the separation of pyrolyzates. Due to the wide range of fragment size that may be encountered, temperature ramps are utilized. When selecting oven parameters, several variables must be taken into consideration including the molecular weight range of fragments, the resolution required between peaks, the potential for sample carryover, and the overall run time.

4.5.2.4 The choice of column is dependent upon the polarities of pyrolyzates that are being considered. Numerous column lengths, bore diameters, and stationary phase combinations are available. A variety of column polarities can be used for Py-GC applications.

4.5.2.5 Due to the variety of polarities of pyrolyzates generated from a paint sample, the following should be considered during column selection. A high polarity column provides good resolution for isocyanates and acids formed during pyrolysis. However, they are subject to lengthy run times (approximately 45 minutes) and permanent retention of very high polarity pyrolyzates such as phthalic anhydride. A low polarity column provides adequate resolution for many paint pyrolyzates including phthalic anhydride; however, it provides poor resolution for high polarity and small sized pyrolyzates as well as acids formed during pyrolysis. A medium polarity column can be used as a compromise; however it is also subject to long run times.

4.5.2.6 The most commonly used columns for general Py-GC applications are polydimethylsiloxane-based capillary columns of at least 15 meters in length.

4.5.2.7 Various detectors are available for use with gas chromatographic systems. Some detectors have very specific uses and will not be discussed here. The two most common detectors for use with Py-GC include the flame ionization detector (FID) and mass spectrometer (MS).

4.5.2.8 The flame ionization detector is capable of detecting a broad range of combustible pyrolyzates. It is relatively inexpensive, has a large linear dynamic range, and can therefore handle a wide range of sample sizes. In this respect it is not easily susceptible to being overloaded with sample. These attributes make it a common detector for gas chromatographs. Identifications and comparisons with data from an FID are based on retention times of peaks and

the appearance of overall pyrogram patterns. Significance of comparisons and identifications with this type of detection can be enhanced when two columns of differing polarities are used simultaneously (Saferstein and Ostberg).

4.5.2.9 Various types of mass spectrometers are available for use as GC detectors. The choice of mass spectrometer is dependent upon various factors including cost and type of analysis being performed. A discussion of the various types of mass spectrometers is beyond the scope of this document.

4.5.2.10 Several different types of ionization sources are available for use. Of the two most common sources in forensic laboratories, chemical ionization and electron ionization, the latter tends to be more useful for the applications discussed in this guide. The mass spectra that are produced often contain a large amount of structural information that can aid in identifying the pyrolysis products.

4.5.2.11 Mass spectral analysis can also be used to extract specific information from the data. By selecting ions of interest, classes of compounds can be selectively viewed and searches for specific compounds are possible.

5.0 SIGNIFICANCE AND USE

5.1 Pyrograms generated from Py-GC can be used to compare questioned and known paint samples and to identify major constituents. Classification entails analyzing reference standards and empirically assigning peaks in the pyrogram.

5.1.1 The pyrolysis process breaks macromolecular structures into smaller, more volatile units and releases smaller compounds from the complex binder matrix.

5.1.2 The gas chromatograph serves as a method for the separation and detection of the fragments and compounds formed/released during the pyrolysis process.

5.1.3 The mass spectrometer has the potential for identification of paint components. It should be noted that the pyrolyzates produced are not necessarily the same materials that were originally added in the manufacturing process prior to polymerization. The mass spectrometer also has the ability to resolve co-eluting components and provide mass fragmentation patterns for both compounds.

5.1.4 The reconstructed total ion chromatogram looks similar to and provides the same information as a pyrogram from conventional Py-GC analysis. However, it also often provides confirmation of peak identities that can aid in classification of the type of polymer (e.g., acrylic or epoxy) or additive and permit identification of the chemical differences between differing compositions (methyl methacrylate vs. butyl acrylate). Considering the complexity of a pyrogram, this additional information should not be construed as an improvement in discrimination power.

5.1.5 Narrow bore capillary columns used in Py-GC typically require higher injection port split ratios to avoid over-loading of the column. These higher split ratios result in reduced detection of minor pyrolyzates, which in turn reduces the amount of thermal fragmentation information acquired from the pyrolysis process. Py-GC systems using flame ionization detectors can employ medium bore capillary columns that can sustain much higher sample loading. This may permit the use of smaller sample sizes and/or the detection of minor pyrolyzates, often having peak areas less than 0.1 percent of the total pyrolyzate. It should be noted that if a medium bore column is used, a decrease in resolution should be expected.

5.1.6 The use of two independent chromatographic columns (one high polarity and one low polarity) in Py-GC systems may provide improved resolution and discrimination over that obtained from a single column. (Saferstein & Ostberg and Ryland, Jergovich, Kirkbride).

6.0 SAMPLE HANDLING

The general collection, handling and tracking of samples shall meet or exceed the requirements of ASTM E 1492-11 as well as the relevant portions of SWGMAAT's Trace Evidence Quality Assurance Guidelines Document.

6.1 Sample preparation

- 6.1.1 Prior to sampling, efforts should be made to scrape away or otherwise remove any foreign debris or contaminants that are visually observed by stereomicroscopy.
- 6.1.2 For multi-layer paints, the recommended method is to physically separate all layers of the paint for analysis via Py-GC or Py-GC/MS. This method allows the binder from each layer to be effectively characterized.
 - 6.1.2.1 Many forensic paint samples are too small in size to isolate individual paint layers and also provide for replicate analysis. When sample size is limited, it is advisable to prepare replicate samples of intact chips of multi-layered paint systems. Care should be taken to ensure that a similar layer system is prepared for both the known and questioned paints.
- 6.1.3 The sample size required may vary according to sample type, pyrolysis method, column type used, chromatographic conditions and detection method. Typically, sample size should be in the range of 5-100 micrograms. Samples analyzed in replicate and for comparison purposes should be similar in shape and size.

7.0 ANALYSIS

Pyrolysis involves the thermal degradation of the sample in an inert atmosphere resulting in the breaking apart of the polymer system into monomers and other pyrolysis products. The instrument operating conditions should be optimized for pyrolysis (e.g., time and temperature), chromatographic separation (e.g., column selection, temperature programming), and detection.

7.1 Pyrolysis Temperature

- 7.1.1 The pyrolysis unit must pyrolyze the sample at a set temperature and at a reproducible heating rate for a specific duration to ensure reproducibility of the polymer fragmentation.
- 7.1.2 The pyrolysis temperature must allow for complete pyrolysis without causing excessive bond breakage. Excessive fragmentation will render the resulting pyrogram very difficult to interpret and may destroy discriminating higher molecular weight pyrolyzates. A method for checking for complete pyrolysis might include re-running the system at a higher temperature with the original sample in place after the initial run has been completed. If peaks are observed, pyrolysis was not complete and a higher temperature should be used. Repeat this process until complete pyrolysis is attained.

7.2 Gas Chromatograph Parameters

- 7.2.1 The gas chromatograph must have a reproducible temperature profile and a stable carrier gas flow rate.
- 7.2.2 Oven temperature, ramp rates, column type, and gas-flow rates influence the pyrograms obtained. The conditions should be chosen based on the quality of pyrograms produced with regard to peak separation, resolution and reproducibility. Examples of instrumental conditions can be found in a variety of references (Burns and Doolan, Challinor 2001, Plage, et. al., Ryland et. al., Saferestein and Ostberg 1988, Wampler 1997 and 2007, and Wright, et. al.).

7.3 Mass Spectral Range

A scan range should be chosen in order to allow analysis of large molecular weight fragments, while disregarding lower molecular weight fragments that may unnecessarily clutter the mass spectrum.

7.4 Quality control

Quality control procedures should be established and documented by the laboratory.

7.4.1 Sample Containers

7.4.1.1 If a sample container is re-used (e.g. quartz tube, crucible, or metallic foil), it must be cleaned before each use. Each laboratory should develop, document and use a cleaning procedure that demonstrates the container is free of contamination on subsequent runs. One method for cleaning sample containers includes firing them in an apparatus prior to use. A blank run can be performed using a clean container to ensure that no pyrolyzable residues are present.

7.4.1.2 Containers should be discarded if they are damaged or significant residues have built up.

7.4.1.3 When using a platinum coil pyrolysis probe, care must be taken to ensure even spacing of the coils. In addition, the position of the sample inside the sample container should be the same for all samples to ensure reproducibility. In the case of quartz tubes, samples may be retained in position in the tube by the addition of quartz wool or a filler post.

7.4.2 Blanks

7.4.2.1 A system blank must be run prior to analyzing any case samples to ensure that there is no contamination and/or carryover. The system blank should include all aspects of the system.

7.4.2.2 A system blank should also be run in between samples in order to demonstrate that carryover is not occurring.

7.4.2.3 Acceptable maximum peak heights in blank runs should be defined in laboratory procedures.

7.4.3 Performance Check

Prior to use, the performance of the instrument must be verified.

- 7.4.3.1 Instrument verification may be done by analyzing a sample of a standard polymer such as polyethylene, polystyrene, or Kraton 1107.
- 7.4.3.2 The pyrogram produced by the standard should meet the laboratory's established quality control criteria.
- 7.4.3.3 For Py-GC/MS, the mass spectrometer must be tuned using a standard reference compound to ensure optimization of peak shape, accurate mass assignments, and sensitivity.
- 7.4.4 Maintenance and troubleshooting
 - 7.4.4.1 Scheduled routine maintenance procedures are recommended to ensure proper operation of the instrument. They should be performed per individual laboratory procedures. These may include cleaning the detector, reassembling the detector and checking flows, changing GC septa and pyrolysis probe seals, cleaning the injection port, checking/changing glass liners, and performing other cleaning as needed.
 - 7.4.4.2 Maintenance and troubleshooting procedures should be suitably documented. The instrument performance should be checked after maintenance is carried out (e.g., column change or instrument configuration change).

8.0 INTERPRETATION

8.1 Classification/Identification of Paint Components

This document does not purport to set a standard for the identification of individual pyrolyzates. Analysts may find it appropriate to identify certain pyrolyzates or patterns of pyrolyzates in order to classify the binder type or sub-type. The confidence with which such identifications are made will vary depending upon the system used (e.g., single column, two distinct columns, mass spectrometry).

- 8.1.1 Identifications of compounds can be accomplished by comparison to known samples or to a mass spectral library. Reference chromatograms should originate from the same instrument and protocol used in the current analysis. The reference standards used in creating libraries should be traceable.
- 8.1.2 Single component additives (e.g., plasticizers) can often be identified via mass spectral library searches. It is important to note that many of these components are the result of thermal desorption instead of pyrolysis.

8.2 Comparison

- 8.2.1 Pyrograms can be compared side-by-side or using overlays. There are a number of significant factors that should be considered when comparing pyrograms including retention time, shape, relative intensity, or presence/absence of peaks. It may be necessary to assess heterogeneity through the analysis of replicate samples.
- 8.2.2 The presence of additional peaks could be inherent differences between the samples or from extraneous material adhering to the sample. If extraneous material is suspected as the source of the difference, the original sample should be cleaned and additional samples prepared for pyrolysis.

- 8.2.3 For pyrograms to be considered indistinguishable, the retention time of the peaks should have reasonable agreement with each other. In general the positions of corresponding peaks in two or more pyrograms being compared should be within a certain time frame of each other (e.g., ± 0.1 minute, 2%). For sharp peaks, one may use tighter constraints and with broad peaks, greater variation may be acceptable.
- 8.2.4 For pyrograms to be considered indistinguishable, the shape of the peaks should be consistent between comparison samples. The peak width and symmetry should be evaluated. Sample size may affect the peak width and resolution.
- 8.2.5 For pyrograms to be considered indistinguishable, the relative intensities of the respective peaks should be similar between comparison samples. The relative intensity may be affected by the heterogeneity of the sample, sampling, size of sample, or reproducibility of the pyrolysis process.

8.3 Conclusions

Three conclusions can be reached after evaluating and comparing the known and questioned pyrograms: 1) the pyrograms are dissimilar, 2) the pyrograms are indistinguishable, or 3) inconclusive.

- 8.3.1 The pyrograms are dissimilar if there are one or more significant differences in the pyrograms. Significant differences are differences in which the variation between pyrograms cannot be explained other than as differences between samples.
- 8.3.2 The pyrograms are indistinguishable if there are no significant differences in the pyrograms. Differences are not significant if the variation can be explained as something other than differences between samples.
- 8.3.3 An inconclusive determination is one in which constraints of sample size or condition precludes a decision as to whether differences are significant or not.

9.0 DOCUMENTATION

- 9.1 When making comparisons of paint, similarity or dissimilarity in the pyrograms should be noted.
- 9.2 Case notes should include a copy of all of the instrumental data that was used to reach a conclusion. All copies should include a unique sample designation, the operator's name/initials, and the date of analysis.
- 9.3 Case notes should also include a description of the evidence analyzed, the method of sample preparation employed, and the analytical instrumentation used with the operating parameters.
- 9.3.1 The following variables should be included:

Pyrolysis Conditions

- ◆ Pyrolysis unit
- ◆ Interface/Standby temperature
- ◆ Pyrolysis temperature and time
- ◆ Ramp rate (if used)

Gas Chromatography Conditions

- ◆ Instrument used
- ◆ Column used (including length, diameter, coating, coating thickness)
- ◆ Injection port temperature
- ◆ Carrier gas and flow rate
- ◆ Inlet pressure
- ◆ Split Ratio
- ◆ Oven temperature (including initial-final temperatures, ramp rates, durations)
- ◆ Detector type
- ◆ Detector Conditions
- ◆ Interface (transfer line) temperature

9.4 See SWGMAAT's Trace Evidence Quality Assurance Guidelines and Expert Reporting Guideline for further requirements.

10.0 REFERENCES

Blackledge, R. D. Application of pyrolysis gas chromatography in forensic science, *Forensic Science Review* (1992) 4:2-16.

Burns, D.T. and Doolan, K.P. The discrimination of automotive clear coat paints indistinguishable by Fourier transform infrared spectroscopy via pyrolysis-gas chromatography-mass spectrometry, *Anal. Chim. Acta* (2005) 539:157-164.

Challinor, J. M. Forensic applications of pyrolysis capillary gas chromatography, *For. Sci. Int.* (1983) 21:269-285.

Challinor, J.M. Pyrolysis techniques for the characterization and discrimination of paint, In: *Forensic Examination of Glass and Paint: Analysis and Interpretation*, B. Caddy, editor (2001) Taylor and Francis, NY, NY.

Irwin, W. J. *Analytical Troubleshooting: A Comprehensive Guide*. (1982) Marcel Dekker, New York.

Plage, B., Berg, A.-D., and Luhn, S. The discrimination of automotive clear coats by pyrolysis-gas chromatography/mass spectrometry and comparison of samples by a chromatogram library software, *For. Sci. Int.* (2008)177:146-152.

Ryland, S., Jergovich, T. and Kirkbride, P. Current trends in forensic paint examination, *Forensic Science Review*, (2006) 18:2:97-117.

Saferstein, R. and Manura, J. J. Pyrolysis mass spectrometry: A new forensic science technique, *J. of Forensic Sci.* (1977) 22:748-756.

Saferstein, R. and Ostberg, E. Dual Column Pyrolysis Gas Chromatography, *Crime Laboratory Digest* (1988) 15:2:39-43.

Stafford, D. T. Forensic capillary gas chromatography. In: *Forensic Science Handbook* (Vol. 2). R. Saferstein, editor (1988) Prentice-Hall, Englewood Cliffs, New Jersey.

Walker, J. G., Jackson, M. T., and Maynard, J. B. *Chromatographic Systems: Maintenance and Troubleshooting*. Academic Press, New York, 1973.

Wampler, T. P. and Levy, E. J. Reproducibility in pyrolysis: Recent developments, *J. Anal. Applied Pyrolysis* (1987) 12:75-82.

Wampler, T.P., Bishea, G.A., and Simonsick, W.J. Recent Changes in Automotive Paint Formulation Analyzed by Pyrolysis-GC/MS for Identification, (1997) *J. Anal. Applied Pyrolysis* 40:79-89.

Wampler TP, editor. *Applied Pyrolysis Handbook 2nd edition*. (2007) Taylor & Francis Group, Boca Raton, FL.

Wright, D.M., Bradley, M.J., and Mehlretter, A.H. Analysis and discrimination of architectural paint samples via a population study, *For. Sci. Int.* (2011) 209:86-95.