## Appendix C

1. May, R.W. and Porter, J., "An evaluation of common methods of paint analysis," Journal of Forensic Science Society, 15 (2), 1975, pp.137-146.

- Thirty-one household gloss paints; eleven white, ten red of similar colors, ten green of similar colors
- Samples were acquired from ten different British manufacturers supplying the specific colors.
- Samples have binders which vary little, basically o-phthalate pentaerythritol alkyds with some having small proportions of modifiers such as urethanes.
- Compared discrimination capability within color sets of various analytical techniques, including microchemical tests, infrared spectroscopy, pyrolysis gas chromatography, pyrolysis infrared spectroscopy, dc-arc emission spectrography, x-ray diffractometry, and laser spark emission spectroscopy.
- Little correlation in discrimination power between the various techniques, except when there is a unique additive present, such as an antimony trioxide fire retardant.
- Using the seven techniques it was possible to discriminate between all of the reds, all of the greens and six of the whites.
- Reeve, V.C. and Keener, T., "Programmed energy dispersive x-ray analysis of top coats of automotive paint," Journal of Forensic Sciences, 21 (4), pp. 883-907, 1976.
  - Analyzed 140 samples of OEM topcoat automotive paint in situ contained in the 1974 National Bureau of Standards (NBS) Automotive Colors paint collection using X-ray Fluorescence (XRF) analysis.
  - Reported that in only one instance could the authors not discriminate between similarly colored samples.
  - Manufacturer's information along with information from the NBS confirmed that the two samples did indeed originate from the same source, acting as an internal control for Type I errors.
- 3. Howden, C.R., Dudley, R.J. and Smalldon, K.W., "The non-destructive analysis of single layered household paints using energy dispersive x-ray fluorescence spectrometry," Journal of the Forensic Science Society, 17, 1977, pp.161-167
  - Sample sets the same as used in the May and Porter study (1975)
  - All green discriminated by visual comparison of XRF spectra
  - All red discriminated by visual comparison of XRF spectra and peak ratio comparison (used for two pairs)
  - All white discriminated except for one pair
- 4. Laing, D.K., et al, "The discrimination of small fragments of household gloss paint by microspectrophometry," Forensic Science International, 20, 1982, pp. 191- 200.
  - Evaluated discrimination power on twelve sets (10-15 samples in each set) of similarly colored household gloss paints obtained from different manufacturers.

- The paints were supplied to a specific color standard for each color group
- Although the paint colors could typically be discriminated by visual examination of large samples, discrimination became difficult on 0.5 mm. x 0.5 mm samples viewed side by side under the stereomicroscope.
- Discrimination power for the respective color groups of the laboratoryprepared paint samples using numerically compared reflectance microspectroscopy was typically 96% or better.
- 5. Fukuda, K., "The pyrolysis gas chromatographic examination of Japanese car paint flakes," Forensic Science International, 29 (3,4), 1985, pp. 227-236.
  - 78 Japanese automotive paints topcoats only (1981 vintage)
  - 31 white, 31 silver metallic, 16 clear coats (worst case scenario)
  - Categorized based on order of four major PGC peaks only packed Carbowax 20M column
  - Of the 31 whites, 22 categories discovered
    0 15 categories of 1 each
  - Of the 31 silver metallics, 17 categories discovered
    - 9 categories of 1 each
  - Of the 16 clear coats, 13 categories discovered
    - 10 categories of 1 each
- 6. Ryland, S.G., "Infrared microspectroscopy of forensic paint evidence," In <u>Practical</u> <u>Guide to Infrared Microspectroscopy</u>, Humecki, H.J., ed., Marcel Dekker, Inc.,1995, pp. 222-232.
  - Three "worst case scenarios" given where IR and/or PGC differentiate automotive topcoats of the same color and general binder type designated to be used on the same make and approximate year of vehicle but manufactured by different paint companies.
- 7. Ryland, S.G., et. al., "Discrimination of 1990s original automotive paint systems: A collaborative study of black nonmetallic base coat/clear coat finishes using infrared spectroscopy," Journal of Forensic Sciences, 46 (1), 2001, pp. 31-45.
  - Eight different laboratories analyzed nine clearcoat over black automotive paint samples using Fourier Transform infrared spectroscopy (FTIR). Black was chosen as a worst-case example in order to avoid any contribution from coloring pigments.
  - The samples were acquired from General Motors Corp. and were selected to represent the various types of clearcoat and basecoat binder formulations in use during the early 1990s.
  - Finishes included clearcoat/basecoat systems being supplied by the three major automotive paint suppliers in the US (BASF, DuPont, and PPG).
  - All eight laboratories were able to visually discriminate the infrared spectra from the nine different systems, some being of the same binder class.

- B. Govaert, F. and Bernard, M., "Discriminating red spray paints by optical microscopy, Fourier transform infrared spectroscopy, and X-ray fluorescence," Forensic Science International, 140 (1), 2004, pp. 61-70.
  - Fifty-one different red spray paints acquired from several different European suppliers were compared with one another using optical microscopy, Fourier Transform infrared spectroscopy (FTIR) and X-ray fluorescence spectroscopy XRF).
  - 98.8% of the 1,275 possible pairs were discriminated using these techniques.
- Buzzini, P. and Massonnet, G., "A market study of green spray paints by Fourier transform infrared (FTIR) and Raman spectroscopy, Science and Justice, 44 (3), 2004, pp. 123-131.
  - 40 different green spray paints equaling 780 possible pairs
  - 95% of the possible pairs were discriminated by FTIR
  - 91% of the possible pairs were discriminated by Raman
  - 98% of the possible pairs were discriminated by a combination of both techniques
  - Raman spectroscopy permitted identification of many of the organic pigments
- Bell, S., Fido, L.A., Speers, S.J., and Armstrong, W.J., "Rapid forensic analysis and identification of "Lilac" architectural finishes using Raman spectroscopy," Applied Spectroscopy, 59 (1), 2005, pp. 100-108.
  - Fifty-one lilac-colored household paints were inter-compared using Raman spectroscopy.
  - The paints differed in either manufacturer, gloss, or tint.
  - All of the 1,275 possible pairs were discriminated by manually measuring band intensities or by creating and searching of spectral libraries.
- 11. Bell, S., Fido, L.A., Speers, S.J., and Armstrong, W.J, Spratt, S., "Forensic analysis of architectural finishes using Fourier transform infrared and Raman spectroscopy, Part II: White paint," Applied Spectroscopy, 59 (11), 2005, pp. 1340-1346.
  - Reportedly the first comparative study of FTIR and Raman spectroscopies for white paint.
  - 51 prepared single layers of white paint were able to be classified into distinct groups or as individual samples.
    - FTIR provided five groups and four individual samples
    - $\circ\,$  Raman provided seven groups and six individual samples
  - Resin type and inorganic pigments/extenders were the basis for discrimination

- Major advantage of Raman is the high level of spectral reproducibility allowing for even relatively small spectral differences to discriminate samples
  - Half of the white samples were not discriminated by FTIR
  - Differences in the Raman data (relative to the experimental uncertainty) discriminated these samples into smaller, distinct groups
- 12. Eyring, M., Lovelace, M., and Sy, D., "A study of the discrimination of some automotive paint films having identical color codes," proceedings of the NIJ/FBI Trace Evidence Symposium, August 13-16, 2007, Clearwater Beach, FL.
  - "Worst-case scenario" discrimination study controlling the color of nondecorative flake paints
  - 34 red samples, including Ford's color code E-4 and Chrysler's code PR-4
  - 70 white samples, including Ford's color code WT and YZ, Hyundai's code NW, and Chrysler's code PW-7
  - Some sets from the same plant within the same year
  - Many sets from the same plant over a 5 year span
  - All 104 samples distinguished by microscopic, IR (micro ATR), MSP, SEM-EDS comparisons
  - IR discriminated the overwhelming majority of samples not discriminated by microscopic examination (90%)
    - 3 pairs of red Chrysler color code PR-4 and one pair of Ford color code E-4 required the addition of MSP to distinguish each pair (97%)
    - 3 samples of white Ford color code WT were indistinguishable by microscopic, IR, and MSP and required SEM-EDS to distinguish them
- 13. Roux, C., Inkster, J., Maynard, P, Ferguson, B., "Intra-sample vs inter-sample variability in architectural paint," proceedings of the NIJ/FBI Trace Evidence Symposium, August 13-16, 2007, Clearwater Beach, FL.
  - Discrimination study on architectural paint samples differing either in manufacturer, gloss, binder type or batch.
  - Nine different products were sampled with anywhere from 2 to 14 different batches on each. Two of the nine were tinted and the remaining seven were white.
  - Samples were inter-compared using microscopy, microspectrophotometry, Fourier Transform infrared spectroscopy (FTIR), micro X-ray fluorescence spectroscopy (µXRF), and pyrolysis gas chromatography-mass spectrometry (PyGC-MS).
  - All of the different products were differentiated while the batches generally were not.
- 14. Plage, B., Berg, AD., and Luhn, S., "The discrimination of automotive clear coats by pyrolysis-gas chromatography/mass spectrometry and comparison of samples by a chromatogram library software," Forensic Science International, 177, 2008, pp.146-152.

- A discrimination study of twenty-five colorless automotive clear coats populating eight different groups having very similar infrared spectra.
- The FTIR groups consisted of 7 samples in one, 5 in another, 3 in another, and 2 in the remaining five groups.
- 19 of the samples were discriminated from all others in the data set
- There were three pairs of samples that could not be differentiated by Py-GC-MS
- Hence 99 % of the 300 possible pairs were discriminated using only Py-GC-MS
- 15. Ryland, S., "Discrimination of retail black spray paints," Journal of the American Society of Trace Evidence Examiners, 1 (2), 2010, pp.109-126.
  - A discrimination study of seventy-one black household spray paints
  - Microscopy, Fourier Transform infrared microspectrometry, scanning electron microscopy in conjunction with energy dispersive X-ray spectrometry and pyrolysis gas chromatography were used to intercompare all possible pairs.
  - The final discrimination power for the 2,485 possible pairs was 99.4 %.
  - The fourteen indistinguishable pairs consist of two groups of four and two groups of two
  - Three of the four groups contain apparent second party vendors.