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Measurement and Variation of UV Absorbers within Multi-Year Samples of Automotive Clear Coat Paint

ABSTRACT

Clear coats are routinely encountered in forensic automotive paint analysis. A methodology is proposed that utilizes multiple instruments (with a focus on microspectrophotometry) while employing a minimum amount of sample. Also, a trend in degradation in UV absorbers across the width of a clear coat layer is described.

INTRODUCTION

Clear coats have become ubiquitous in automotive paint since their introduction in the early 1970's. In addition to the role of the clear coat in providing protection to the vehicle from nicks and scratches, ultraviolet (UV) light absorbers are also added to protect the color coat from degradation [1,3]. The typical classes of UV absorbers added to clear coats are 2-hydroxyphenyl-S-triazines and 2-hydroxyphenylbenzotriazoles. These compounds are designed to capture UV light and, through photochemical processes, prevent the light from reaching the underlying color coat (*Figure 1*) [2,3].
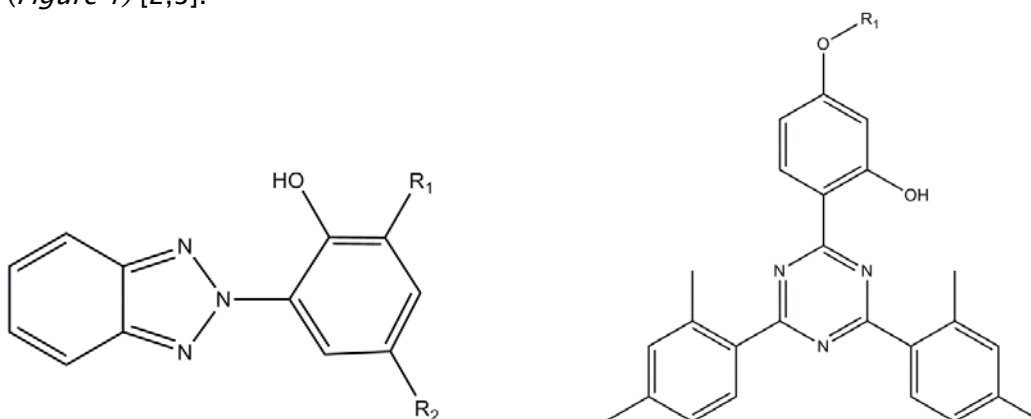

Figure 1 – Example structures of hydroxyphenyl-S-triazines (left) and hydroxyphenylbenzotriazoles (right) [3].

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These compounds are generally used along with hindered amine light stabilizers (HALS) to protect the color coats (*Figure 2)* [3].
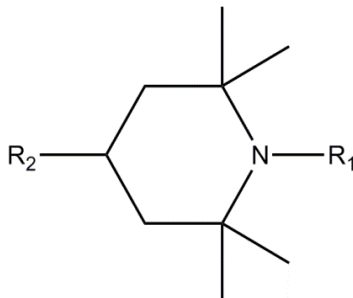

Figure 2 – Example structure of a hindered amine light stabilizer (HALS) [3].

Over time, the degradation of UV absorbers in a clear coat occurs due to exposure to the environment [4].   This degradation should be more pronounced near the surface of the clear coat. Because of this the concentration of UV absorbers should be seen to vary, with a higher concentration near the color coat and a lower concentration near the environment. In order to observe this trend, a UV–visible microspectrophotometer (MSP) can be employed to perform selective analysis of the UV absorbers in the clear coat at different depths within the layer.

Forensic examination of clear coats has been performed using a combination of Fourier transform infrared spectroscopy (IR) and pyrolysis gas chromatography / mass spectrometry (Py–GC/MS) [4,6,7]. Discrimination and association between clear coats can be achieved using these methods, but we hope to show that UV–Visible microspectrophotometry can be added to these methods to aid in clear coat comparisons.   It can provide data throughout the depth of a layer and contribute useful information to the analysis.

This paper reports the results of a one day research project at the NWAFS Fall 2011 Meeting with some additional work that was completed at a later date. The goal is to show how the MSP can be employed during analysis of clear coats using a methodology that includes a combination of stereomicroscopy, IR, and UV–Visible microspectrophotometry. This methodology can provide a large amount of comparative data quickly.

METHODS

Samples from several Washington State Patrol (WSP) Ford Crown Victorias were collected for use in this study. Samples from model years of 2000, 2002–2005, 2007, and 2008 were selected for analysis. All of the selected samples were from vehicles manufactured

in the same facility with the same paint color. The Vehicle Identification Number (VIN) for each of the selected vehicles was checked using VINassist® (National Insurance Crime Bureau, Des Plaines, IL) to verify the year and plant of manufacture (*Figure 3*).

Year	VIN	Area Sampled	Plant
2000	2FAFP71W5YX140503	Trunk	St. Thomas, Talbotville, Canada
2002	2FAFP71WX2X118648	Hood	St. Thomas, Talbotville, Canada
2003	2FAFP71W93X132526	Hood	St. Thomas, Talbotville, Canada
2004	2FAHP71W34X121001	Left Rear Roof Post	St. Thomas, Talbotville, Canada
2005	2FAHP71W45X143008	Roof	Talbotville, Canada
2007	2FAHP71W37X132746	Left Rear Roof Post	St. Thomas, Talbotville, Canada
2008	2FAHP71V08X178155	Left Rear Roof Post	St. Thomas, Talbotville, Canada

Figure 3 – Samples used in this study. Talbotville, Canada is the same plant as St. Thomas, Talbotville, Canada. The names are taken directly from VINassist®.

The samples were first mounted in a fast setting (less than 5 minutes) epoxy (Double/Bubble, Hardman®, Belleville, NJ). This was completed by applying a release agent to a mold, then applying the epoxy and embedding the paint sample. The epoxy sample was allowed to sit for at least an hour, and then cross-sectioned using a microtome (American Optical, Buffalo, NY) at 7-microns thick.   Each sample was mounted separately due to the number of samples being analyzed.   Previous research has suggested cross section thicknesses of 20 microns,[2] but current instrumentation for UV microspectroscopy is able to analyze thinner cross-sections. Thinner cross-sections are able to be used on multiple instruments, even if the instruments are older. The prepared cross-sections were checked to make sure they were a consistent thickness and layer structure (i.e. clear coat, color coat, under coat) using a stereomicroscope. They were then placed on a potassium bromide window and analyzed with an IR microspectrometer (Perkin-Elmer, Waltham, MA) in transmission mode. These same cross sections were then mounted in glycerin on a quartz microscope slide with quartz coverslip and analyzed on an MSP (CRAIC Technologies, San Dimas, CA) in transmission mode.

In order to ensure consistency with regard to the UV absorbers across the various model years, an MSP spectrum was taken from each of the selected samples at an area close to the color coat. This would be the depth at which the clear coat would be expected to have the least possible degradation. In order to observe the changes in UV absorber concentration through a layer, spectra were taken from closest to the color coat and moving outwards towards the environment (*Figure 4*).
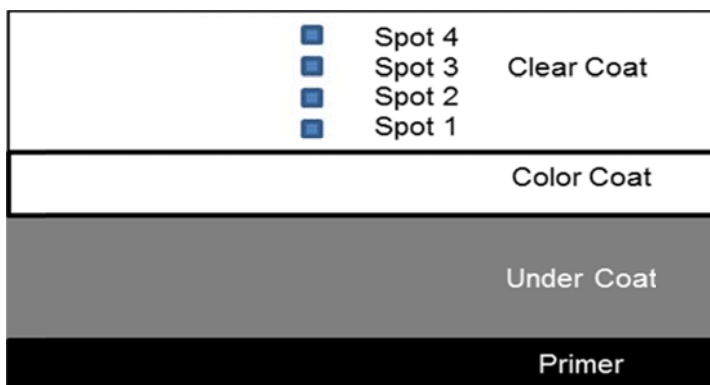

Figure 4 – Example of a paint chip cross-section showing how the clear coat was sampled for MSP analysis within a layer. Spot 1 is closest to the color coat and Spot 4 is closest to the environment.

MSP data showing the consistency in UV absorbers for all samples and the decrease in UV absorbance throughout the depth of a layer for one sample, as well as IR data for all samples were collected at the NWAFS Fall 2011 Meeting in Tacoma, WA. Only one IR spectrum was taken for each manufacturing year. Further data showing the decrease in UV absorbance in a layer for all samples were collected post-meeting in the WSP Seattle Crime Lab with the same model MSP and similar experimental conditions, but with freshly prepared cross-sections made on a different microtome (American Optical, Buffalo, NY).

RESULTS AND DISCUSSION

Analysis using the methodology described above is quick, efficient, and allows the same sample to be used with different techniques. The data from the Fall Meeting display consistency in the IR spectra (Figures 5 and 6). Although there are slight differences present in the IR spectra of the different samples, they are not substantive enough to

eliminate one sample from another during comparison based on only having a single spectrum for each. It may have been possible to account for the variances in the transmission line and possible contributions of components from the color coat with additional data collection as well as discriminate between samples with adequate replicates, but this was not possible within the time constraints.
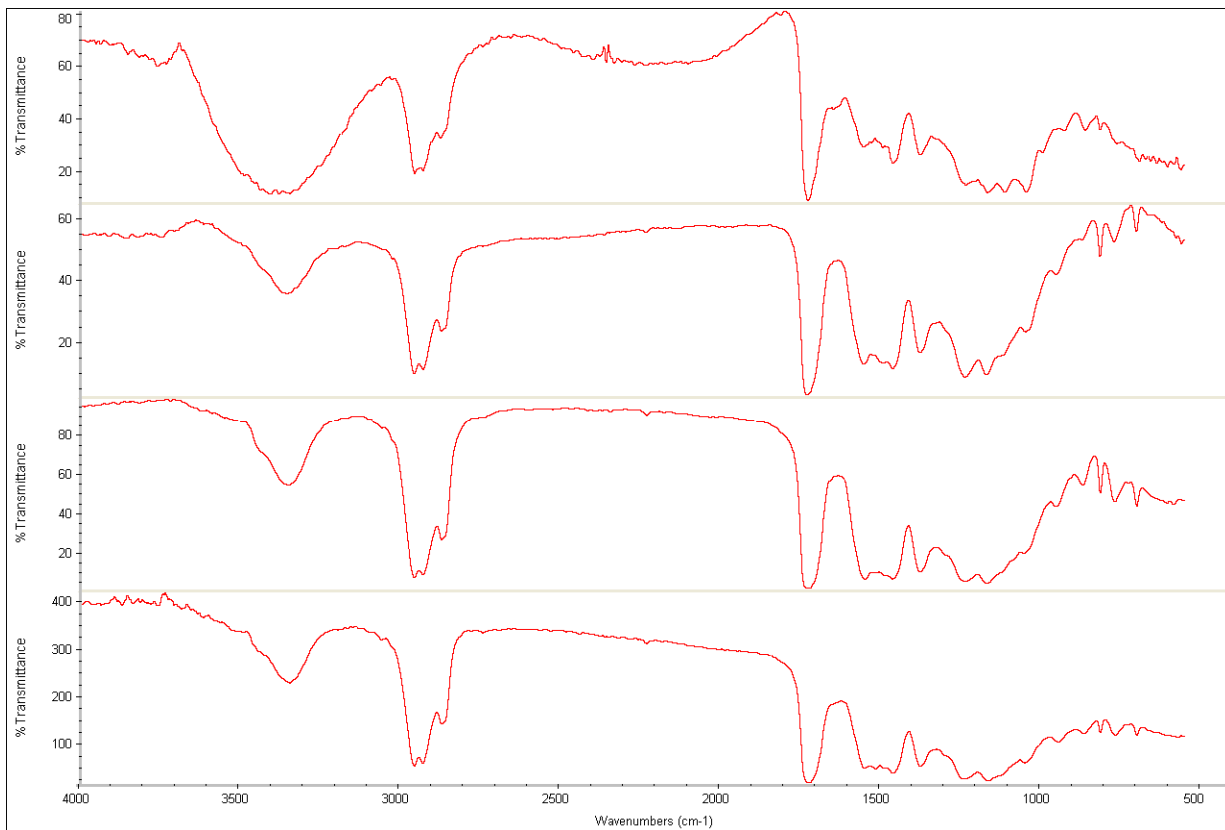

Figure 5 – IR Data collected at the NWAFS Fall 2011 Meeting. This set includes (from top to bottom) 2000, 2002, 2003, and 2004.
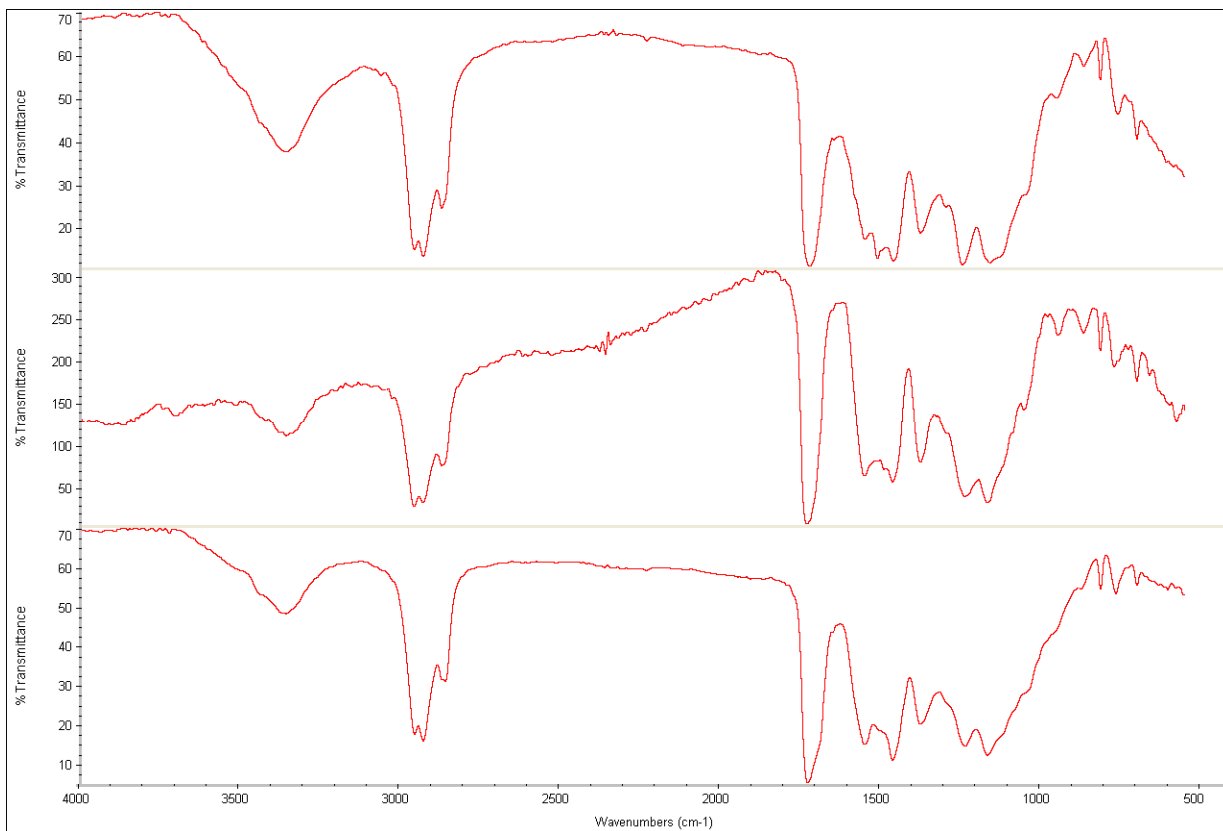
Figure 6 – IR Data collected at the NWAFS Fall 2011 Meeting. This set includes (from top to bottom) 2005, 2007, and 2008.

The MSP data display a similar trend. The different years display a consistency in peak shape and peak location. Variation in absorbance is due to the similar components having different relative concentrations (Figure 7).
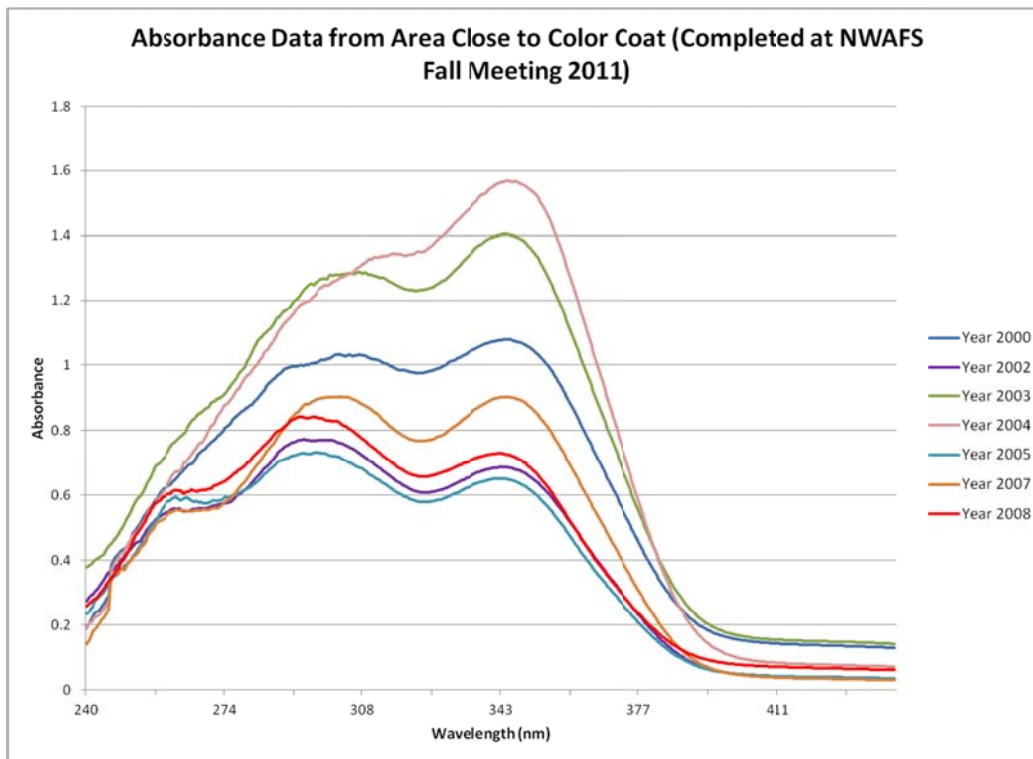
Figure 7 – MSP Data taken at Spot 1 at the NWAFS Fall 2011 Meeting taken close to the color coat.

There is a decrease in the amount of UV absorption throughout a clear coat layer. This was first measured during the Fall Meeting in the sample from 2002 (Figure 8). Subsequent to the Fall meeting the samples were retested by sampling four points in the clear coat as previously described. A decrease in UV absorption through a clear coat layer was produced for each year. Examples of the degradation include the 2002 data (same sample as the NWAFS data) and the 2000 data (Figures 9 and 10).
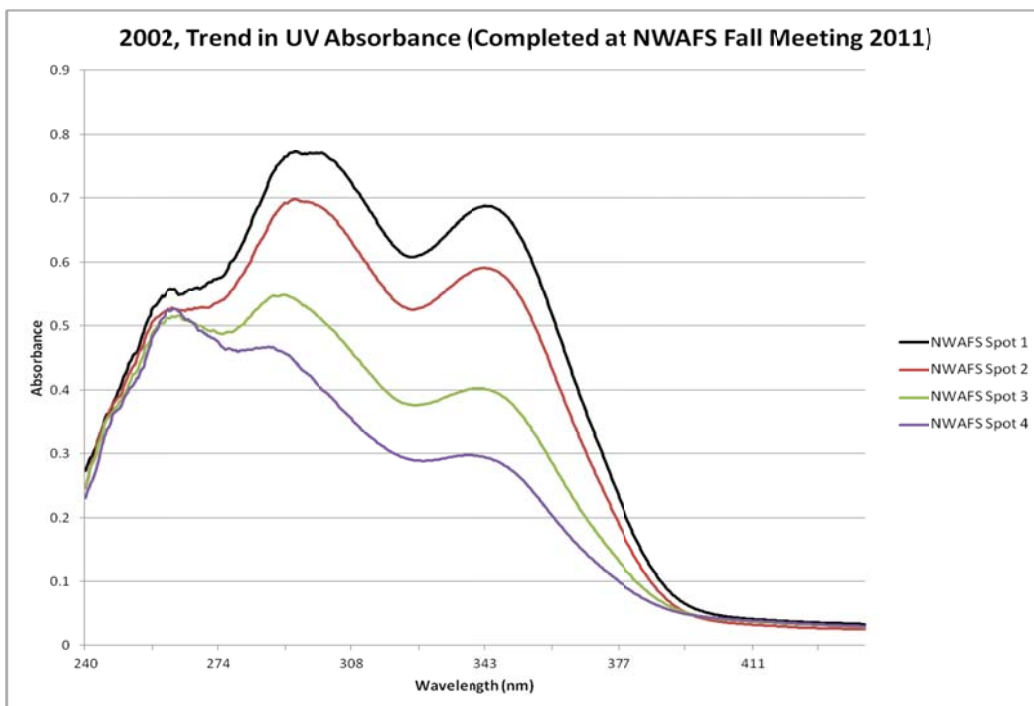
Figure 8 – Data for the 2002 sample taken at the NWAFS Fall 2011 Meeting. Data were from closest to the color coat (Spot 1) to closest to the environment (Spot 4). The degradation of the UV absorbers in the clear coat is shown by the decrease in the absorbance values.
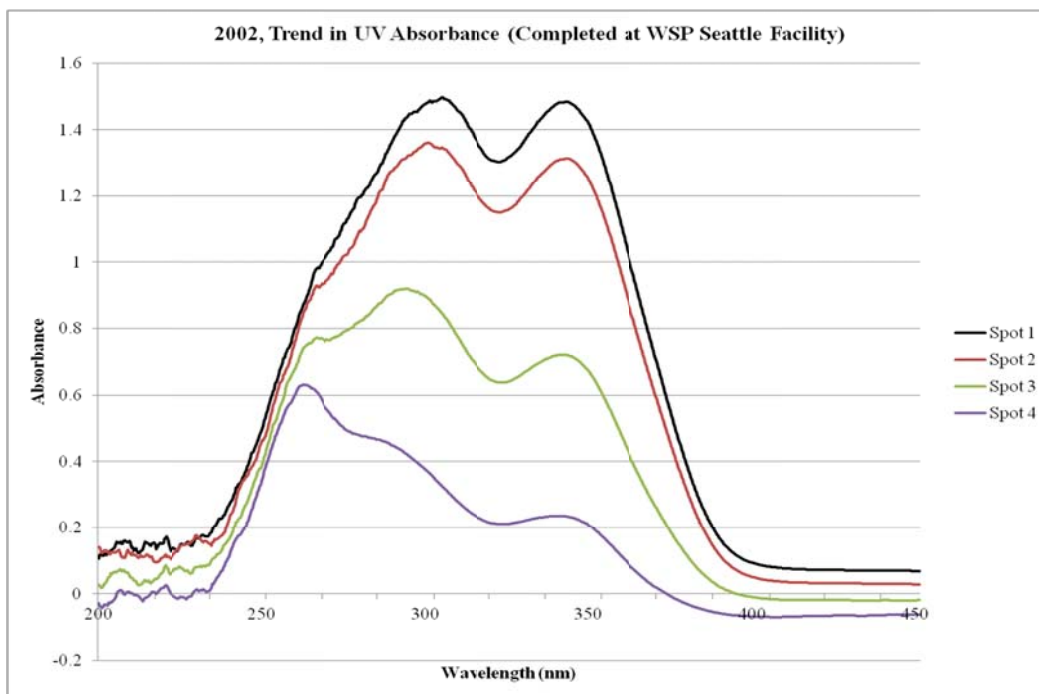

Figure 9 – Data for the 2002 sample taken at the WSP Seattle Crime Lab. Data were from closest to the color coat (Spot 1) to closest to the environment (Spot 4).
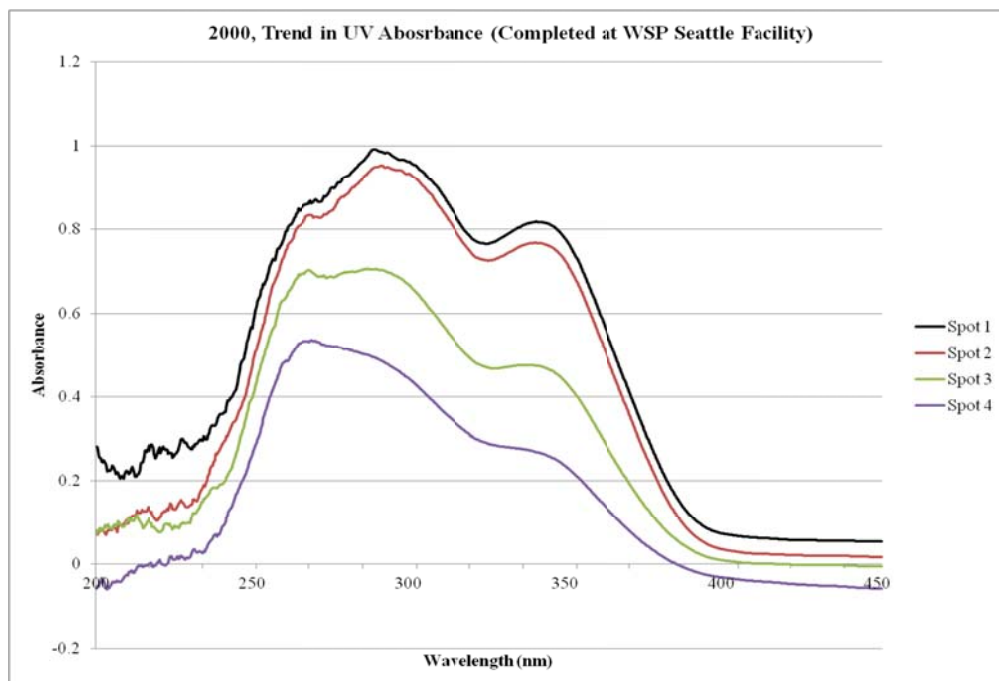
Figure 10 – Data for the 2000 sample taken at the WSP Seattle Crime Lab. Data were from closest to the color coat (Spot 1) to closest to the environment (Spot 4).

The data shows a decrease in UV absorption in a clear coat as the sampling area is moved closer to the environment rather than the color coat. This trend is due to the interaction of sunlight with the UV absorbers previously discussed.[4] Although it may be expected that a starker decrease in UV absorbers should be seen in 2000 than in later years, this will not always be the case due to factors such as the environment which the car was used in and the amount of time the vehicle was in service.

It is important to note that the sampling throughout the layer at differing depths can make a large difference in what data is collected. Even samples taken close to each other can exhibit differences in relative concentration as was seen with the 2002 sample. If a sample is taken close to the nominally exposed surface for a questioned sample and close to the color coat for a known sample, it may lead to a perceived difference between two samples that actually share a common origin.

CONCLUSIONS

The methodology developed for sampling and analyzing clear coats is quick and efficient. In one day, a series of paint chips were cross-sectioned using a microtome, and then analyzed using a series of stereomicroscopic, IR, and MSP examinations. This series could be adapted to include additional instrumentation after MSP including scanning electron microscopy in conjunction with energy dispersive X-ray spectrometry. An examiner would be able to obtain a wide variety of data with only a trace amount of material; however, cross-sectional IR analysis of thinner color coats can be problematic due to the reduced signal-to-noise and diffraction effects caused by the requisite smaller apertures. Analysis is dependent on multiple factors including the available equipment in the laboratory, the consistency in the sample preparation, and, critically, sampling location within a layer. Any inconsistency in the sampling and analysis can possibly lead to variations in results and potential false eliminations.

The data collected clearly show a degradation of UV absorber that occurs through a clear coat layer. Questions that will be investigated in the future are whether this trend is consistent for different areas on the same panel of one vehicle and whether there is variation in clear coat absorption between different parts on the same vehicle.

ACKNOWLDGEMENTS

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