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Survey on batch-to-batch variation in spray paints: A collaborative study

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ABSTRACT

This study represents the most extensive analysis of batch-to-batch variations in spray paint samples to date. The survey was performed as a collaborative project of the ENFSI (European Network of Forensic Science Institutes) Paint and Glass Working Group (EPG) and involved 11 laboratories. Several studies have already shown that paint samples of similar color but from different manufacturers can usually be differentiated using an appropriate analytical sequence. The discrimination of paints from the same manufacturer and color (batch-to-batch variations) is of great interest and these data are seldom found in the literature. This survey concerns the analysis of batches from different color groups (white, papaya (special shade of orange), red and black) with a wide range of analytical techniques and leads to the following conclusions.

Colored batch samples are more likely to be differentiated since their pigment composition is more complex (pigment mixtures, added pigments) and therefore subject to variations. These variations may occur during the paint production but may also occur when checking the paint shade in quality control processes. For these samples, techniques aimed at color/pigment(s) characterization (optical microscopy, microspectrophotometry (MSP), Raman spectroscopy) provide better discrimination than techniques aimed at the organic (binder) or inorganic composition (fourier transform infrared spectroscopy (FTIR) or elemental analysis (SEM – scanning electron microscopy and XRF – X-ray fluorescence)).

White samples contain mainly titanium dioxide as a pigment and the main differentiation is based on the binder composition (C–H stretches) detected either by FTIR or Raman. The inorganic composition (elemental analysis) also provides some discrimination.

Black samples contain mainly carbon black as a pigment and are problematic with most of the spectroscopic techniques. In this case, pyrolysis-GC/MS represents the best technique to detect differences. Globally, Py-GC/MS may show a high potential of discrimination on all samples but the results are highly dependent on the specific instrumental conditions used.

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Finally, the discrimination of samples when data was interpreted visually as compared to statistically using principal component analysis (PCA) yielded very similar results. PCA increases sensitivity and could perform better on specific samples, but one first has to ensure that all non-informative variation (baseline deviation) is eliminated by applying correct pre-treatments. Statistical treatments can be used on a large data set and, when combined with an expert's opinion, will provide more objective criteria for decision making.

1. Introduction

Paint traces are regularly encountered in criminalistics cases, as coated materials are all over our surroundings and paint traces are easily transferred during contact between coated objects. Hence, the evidential value of any trace is frequently estimated within a Bayesian framework, regarding the chance of finding a random match with the paint trace [1]. This is estimated with surveys of paint from different brands, analyzed by various forensic analytical techniques [2–5]. However, when two samples are left undifferentiated, it leads to questions relating to the discrimination of paints within a single brand (batch): can any two samples from two distinct production batches be discriminated by standard forensic techniques? The industry acknowledges that adjustments are performed by adding small amounts of concentrated single-pigment solutions. These single-pigments solutions can be of the same origin as initial pigments but can also be totally different. Further, a drift in controlled color is corrected using pigments of the opposite color to adjust the tint [6]. The differentiation of paints at a batch level has not been extensively studied and most of the previous studies focused on automobile samples [7]. Bell et al. [8] analyzed Raman spectra of architectural lilac paints, including two sample sets of batches of different colors. They observed that the predominant source of variation is the ratios between peaks (rutile ratioed to other components). At conclusion, they point out the need for extensive studies to establish the extent of batch-to-batch variation within the general population. Inkster et al. [9] used a complete sequence of examination on 14 batches of architectural white paints (optical microscopy, MSP, FTIR, μ-XRF and Py-GC/MS). One sample could be distinguished, though the comparison steps were only qualitative. In an additional study in two parts, Bell et al. [10,11] compared the discrimination possibilities of FTIR and Raman spectra on resins and white paints. They highlighted large differences in the Raman spectra and showed the possibility of discriminating based not only on the bands they contain (qualitatively) but also on their relative intensities (characterizing within-group variation). This was not possible with FTIR because the experimental uncertainty in the measurements was of similar magnitude to the within-group differences between the resins.

The present article tries to fill that gap with an extensive study of batch-to-batch variations to determine if a quantitative distinction between paints of the same brand can be achieved. This work was performed as part of a collaborative study from the ENFSI Paint and Glass Working Group (EPG). Four color sets of spray paint samples (23 samples in total) were collected directly from the manufacturers and were certified to belong to distinct batches. The samples were analyzed by the 11 laboratories participating in the project utilizing 6 different analytical techniques (e.g. optical microscopy, infrared spectroscopy, Raman spectroscopy, pyrolysis gas chromatography–mass spectrometry, elemental analysis and microspectrophotometry). To check reproducibility of the results, most of the analytical techniques were used at least twice in different laboratories. The results were evaluated in terms of undiscriminated pairs of samples, by visual inspection of the data and by application of multivariate statistical techniques to the infrared and Raman spectroscopies and MSP data.

This survey will provide information about the techniques that offer the highest discrimination for batch to batch samples of various colors. It also addresses the improvement one could expect by using multivariate statistical techniques particularly on spectroscopic data such as infrared, Raman or MSP spectra.

2. Materials and methods

The procedure described hereafter is meant to give an overview of the project development and the procedures followed to check the reproducibility of results. A total of 6 analytical techniques were divided among all the participants. Due to the complex composition of paint, techniques aiming at the characterization of different components were chosen in order to have an overview of both organic and inorganic content.

2.1. Samples

A total of 23 spray paint samples corresponding to 4 different colors (black, white, papaya (special shade of orange) and red) were collected directly from manufacturers. 17 samples were distributed to laboratories in 2010 with six more samples added in 2011. All samples within a color group are commercially available under the same brand and type but represent different batches, meaning they were produced at the same plant but during different time periods. Table 1 presents the samples used.

Each paint sample was sprayed on glass slides from a distance of about 30 cm. Spray cans were shaken for 3 min before their deposition onto the slides. 11 independent sets of samples were prepared by one laboratory and sent to all the other laboratories for analysis.

2.2. Methods

Table 2 summarizes the instrumentation and parameters used by each laboratory. No recommendations on the instrumental conditions were given; each laboratory measured the samples according to their own procedures. The pyrolysis GC/MS measurements were only completed for the 2010 sample set. The sample preparations for each technique were as followed:

Microscopy: Two preparation techniques were used: (1) Paint samples were rolled flat on a glass slide, cleaned with ethanol and dried (10 microns thickness) then they were either observed with no mounting media or mounted in Entellan with coverslip. (2) Samples were deposited on black gelatin lifts without coverslip for reflectance observations. Triplicate of all samples were used and comparison done side by side in a single field of view.

Microspectrophotometry (*MSP*): Paint samples were measured in reflectance directly on their glass slides. No sample preparation was needed.

Infrared spectroscopy (*FTIR*): Measures were made in transmittance on a small amount of paint scraped and flattened then deposited on a KBr pellet.