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Evaluation of infrared spectra analyses using a likelihood ratio approach: A practical example of spray paint examination

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ABSTRACT

Depending on the forensic disciplines and on the analytical techniques used, Bayesian methods of evaluation have been applied both as a two-step approach (first comparison, then evaluation) and as a continuous approach (comparison and evaluation in one step). However in order to use the continuous approach, the measurements have to be reliably summarized as a numerical value linked to the property of interest, which occurrence can be determined (e.g., refractive index measurement of glass samples).

For paint traces analyzed by Fourier transform infrared spectroscopy (FTIR) however, the statistical comparison of the spectra is generally done by a similarity measure (e.g., Pearson correlation, Euclidean distance). Although useful, these measures cannot be directly associated to frequencies of occurrence of the chemical composition (binders, extenders, pigments). The continuous approach as described above is not possible, and a two-step evaluation, 1) comparison of the spectra and 2) evaluation of the results, is therefore the common practice reported in most of the laboratories. Derived from a practical question that arose during casework, a way of integrating the similarity measure between spectra into a continuous likelihood ratio formula was explored. This article proposes the use of a likelihood ratio approach with the similarity measure of infrared spectra of spray paints based on distributions of sub-populations given by the color and composition of spray paint cans. Taking into account not only the rarity of paint composition, but also the "quality" of the analytical match provides a more balanced evaluation given source or activity level propositions. We will demonstrate also that a joint statistical–expertal methodology allows for a more transparent evaluation of the results and makes a better use of current knowledge.

1. Introduction

In forensic cases involving paint, the standard procedure typically involves to analyze both the trace and the known samples with a sequence of analytical techniques. Once the sequence is completed, a decision is taken as to whether or not the two items are differentiable. The major drawback in this practice is that the analytical results are only considered under two outcomes: differentiable or not, whereas the data are continuous and not binary. This can lead to a paradox[2] as shown by Lindley as early as in 1957 [1]. Generally, paint examiners will decide whether the items are different or not, given their knowledge of the analytical techniques, and based on their expert opinion. For example, the appearance of an intense additional peak in one of the items only is often regarded as significant in Infrared or Raman spectroscopies. However, the evaluation of only small variations is much more difficult to appreciate. Different influential factors may contribute to the complex spectral signal and experimental conditions: for example, how the trace was searched and recovered, the heterogeneity of the painted layer (intra-variability), contaminations, or possible degradation of the material might all affect the global spectral shapes, as well as peak intensities. In this situation, the decision to differentiate the trace from a possible source might not be as straightforward to take.

The use of Bayesian evaluation in forensic science has greatly developed over the last half century. The results of many different analytical methods were evaluated and described in the literature using a Bayesian framework, for example refractive index measurements [2], chromatographic techniques [3,4], and elemental analyses [5,6]. However, spectroscopic methods (infrared and Raman principally) were surprisingly put aside until very recently [7,8]. It is only with the development

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[2] Lindley's paradox is a situation where one would – for example – exclude that the recovered paint came from the seized can when using a classical statistical test and say a confidence level of 95%, but when using a Bayesian continuous approach (that takes also into account not only the distance between the measurements, but also the rarity of the characteristics) the results would support the proposition that recovered paint came from the seized can rather than from some unknown spray paint can.

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of chemometrics and statistical analysis that new possibilities arise in disciplines that were initially considered too demanding or where instrumental techniques appeared less adapted to a logical evaluation. This is the case for infrared measurements of paint traces. The Bayesian evaluation of results has been historically applied both as a two-step approach (first comparison, then evaluation, see for example [9]) and as a continuous approach (comparison and evaluation in one step, see [10]). To apply a continuous approach for the comparison of data from a single analytical instrument though, measurements have to be reliably summarized as numerical values linked to the property of interest.

In that sense, the simplest way to assess the instrumental results is where the comparison itself can be evaluated as a likelihood ratio, expressing the probability of observing these results if the two items share a common origin (e.g. recovered trace comes from spray paint X) and the probability of observing these results if the items are from different sources (e.g., recovered trace comes from an unknown spray paint). To do so one uses data acquired within- and between-sample populations [11]. Taking glass as an example, the calculations are often based on refractive indexes. This has been used by Zadora et al. in recent papers [12,13]. The main advantage of refractive index over infrared spectra measurements, is that the statistical comparison is based on a property of interest, which occurrence can be determined (e.g., the probability of observing refractive indexes such as those observed on the fragments in the selected population). For paint traces however, the statistical comparison is generally done by a similarity measure (e.g., correlation, Euclidean distance), but these measures cannot be directly associated to frequencies of occurrence of the chemical composition (binders, extenders, pigments). A two-step evaluation, 1) comparison and 2) interpretation, is necessary for this kind of samples.

For these reasons, likelihood ratio models have sporadically been applied to the evaluation of paint evidence [14]. Buzzini et al. for example presented a two-step approach likelihood ratio model for crowbar burglaries [15], but the use of a continuous approach has also been presented for example by Farmer et al. for white paints isotope analysis [16], and Zieba-Palus et al. for the differentiation of clear-coats by pyrolysis GC–MS [17]. Concerning spectroscopic methods, Martyna et al. used Raman results for the evaluation of automotive paints comparisons [7], as well as Fourier transform infrared spectroscopy (FTIR) for polymers [8]. Except for the latter, the majority of these studies postulate that the spectra/chromatograms are undifferentiable and then the value of this result is assessed through a likelihood ratio. Depending on the instrumental method used, the comparison is rarely challenged or discussed within this logical approach. In this context, although statistical ways of comparing the spectra exist, there have not been many attempts to include them into a wider Bayesian evaluation framework.

Derived from a practical question that arose during casework, we developed a way of integrating the similarity measure between spectra into a more general likelihood ratio formula. This case report proposes the use of a likelihood ratio approach based on the similarity of infrared spectra of spray paints. By not only taking into account the rarity of paint composition, but also the “quality” of the analytical match, it provides a more complete evaluation to the scientist. The evaluation is proposed both given source and activity level propositions depending on the results that need to be assessed. For more on the levels of propositions and the so-called hierarchy of propositions, we refer the reader to [18,19].

In this article, we will thus first present a casework example, and then discuss the framework used for our evaluation. In the third part, we will describe the examinations performed and present the data that are used to assess the value of the results. In the last part of the article, we will evaluate our case results in two situations: paint recovered on a crime scene and paint recovered on a person of interest (e.g., suspect).

2. Materials and methods

2.1. Casework example

The description of the case given to us is as follows: 7 different red spray paint inscriptions were discovered in the morning on different public buildings, some of them still being fresh. A suspect was apprehended shortly after, and had in his possession three cans of red spray paint, as well as different pairs of gloves and a black balaclava. The three spray paint cans were of the same brand and same model, and only the can sizes differed (400 ml or 600 ml).

2.2. Traces and items recovered

The paint from the graffitis (G001–G007) was collected using scalpel blades and put into small pieces of folded paper. A blank was systematically collected at each location.

The three spray paint cans from the suspect were described, the level of filling documented, and reference samples produced by spraying paint onto clean microscopic glass slides after 3 min of shaking (C001–C003).

The suspect's belongings that were confiscated were a black balaclava (P001), one pair of black leather gloves (P002) and four white cotton gloves (P003–P006). The garments were searched using a stereo microscope (magnification of about 200×), and all paint droplets documented (position + color), in case that the suspect would come back on his statement of having used the paint sprays in the last 24 h.

The reference samples used as population of interest were from homemade infrared databases that were built using a collection of spray paint described in [20]. From our database of 74 samples comprising different colors, 31 were red and were thus used for this study.

2.3. Analytical method

All samples were first observed under a DMRX Leica Microscope, using ×20 to ×100 magnifications. The color and optical properties of the paint fragments were documented.

Infrared measurements were performed using a Nicolet 6700 FTIR Spectrometer, equipped with a Nicolet Continuum™ FT-IR Microscope from Thermo Electron Corp. (USA) with a 32× Infinity Reflachromat objective, a mercury cadmium telluride (MCT/A) detector and the software OMNIC 9.1. The sampling method was transmittance on KBr pellets. The measurement parameters were as follows: 150 × 150 μm window size, 4.0 cm^{-1} resolution, 32 co-added spectra, and 4000–650 cm^{-1} range. Seven replicates were measured for each reference spray paint can in order to calculate the statistical distributions. Concerning the paint traces and the graffitis, as many replicates as possible were measured (typically were between 5 and 7 depending on sample size and quality). For most of the paint droplets only 1 or 2 replicates were possible due to sample quantity and FTIR window size requirements.

2.4. Data treatment

All spectra were individually pretreated using a SNV + detrending method with a polynomial order 2. No variable selections were made, except removing regions of poor spectral information in the spectra. The variables kept were: 600–1850 and 2700–3800 cm^{-1} (4773 points). The software Unscrambler X10 (Camo, Norway) was used.

The calculations of correlations and distribution fittings were all made using MATLAB r2012 (Mathworks, USA). For selection of the best similarity measure, Euclidean distance, standardized Euclidean distance, cosine function, Pearson correlation and Spearman correlation were tested for pairwise comparisons of all the samples within the same subpopulation. Pearson correlation and cosine function are expected to give similar results as the calculation is very comparable, the only difference being a mean-centering for the x-values using Pearson correlation.