



The author(s) shown below used Federal funding provided by the U.S. Department of Justice to prepare the following resource:

Document Title:	Characterization and Comparison of Tape Evidence using Elemental Profiling Methods and Chemometric Analyses		
Author(s):	Jose Almirall, Ph.D.		
Document Number:	253891		
Date Received:	October 2019		
Award Number:	2015-DN-BX-K050		

This resource has not been published by the U.S. Department of Justice. This resource is being made publically available through the Office of Justice Programs' National Criminal Justice Reference Service.

Opinions or points of view expressed are those of the author(s) and do not necessarily reflect the official position or policies of the U.S. Department of Justice.

Final Summary Technical Report

Agency: National Institute of Justice

Award No: 2015-DN-BX-K050

Title: Characterization and comparison of tape evidence using elemental profiling methods and chemometric analyses

Principal Investigator:

Dr. Jose Almirall, Professor, Department of Chemistry and Biochemistry and Director Emeritus, International Forensic Research Institute (IFRI) and Director, Center for Advanced Research in Forensic Science (CARFS) Florida International University 11200 SW 8th Street, OE116 Miami, FL 33199 (305) 348-3917 tel (305) 348-4485 fax <u>almirall@fiu.edu</u>





Recipient Organization Address: Florida International University 11200 SW 8th Street Miami, Florida, 33199

Submitting Official:

Mr. Roberto Gutierrez Assistant Vice President for Research Office of Research and Economic Development 11200 SW 8th Street, MARC 430 Miami, Florida, 33199 305-348-2494 gutierrr@fiu.edu

Project Period: 1/1/2016 to 12/31/2018

Report term: Final Summary Technical Report

Submission date: 06/10/2019

Submitting Official Signature:

tom #

Page 1 of 1

Final Technical Report - National Institute of Justice Award No. 2015-DN-BX-K500

Characterization and comparison of tape evidence using elemental profiling methods and chemometric analyses

Submitted by Jose Almirall*, Professor of Chemistry and Biochemistry and Director, Center for Advanced Research in Forensic Science (CARFS), Florida International University

Additional authors and contributors to this research project: Claudia Martinez-Lopez^a, Tatiana Trejos^b, Meghan Prusinowski^b, Sally Coulson^c, John Goodpaster^d, Katherine Igowsky^e, Felix Kuczelinis^f, Andria Mehltretter^g, Edward Pollock^h, Ulrich Simmross^f, Robyn Weimerⁱ, Peter Weis^f,

^a Department of Chemistry and Biochemistry and International Forensic Research Institute (IFRI), Florida International University, Miami, FL 33199, USA
^b Department of Forensic and Investigative Science, West Virginia University, Morgantown, WV 26506, USA
^c Institute of Environmental Science and Research Limited (ESR), Mount Albert Science Centre: 120 Mount Albert Road, Private Bag 92021, Auckland 1142, New Zealand
^d Forensic and Investigative Sciences Program, Indiana University - Purdue University Indianapolis, Indianapolis, IN 46202, USA
^e Minnesota Bureau of Criminal Apprehension, Minneapolis, MN 55106, USA
^f Bundeskriminalamt, KT 42, Wiesbaden, Germany
^g Laboratory Division, Federal Bureau of Investigation, 2501 Investigation Parkway, Quantico, VA 22135, USA
^h Laboratory of Forensic Services, Sacramento, CA 95820, USA
ⁱ Virginia Department of Forensic Science, Richmond, VA 23219, USA

Corresponding author

Acknowledgments

This project was supported by Award No. 2015-DN-BX-050 from the National Institute of Justice, Office of Justice Programs, U.S. Department of Justice to Florida International University. The opinions, findings, and conclusions or recommendations expressed in this article are those of the authors and do not necessarily reflect those of the Department of Justice.

(Cover Page)

Abstract

Adhesive tapes are an important type of evidence related to violent crimes such as the construction of improvised explosive devices and kidnappings as well as involved in other types of common forensic evidence such as drug packaging. The traditional methods of comparison of tape evidence consist of physical and microscopic examination followed by chemical analysis of the organic and inorganic components inherent to the tapes as part of their formulations. The current research evaluates the performance of the conventional methods used in forensic analysis of adhesive tapes (physical and microscopic examination, FTIR, Py-GC-MS, and SEM-EDS) and the more recently developed elemental methods, µXRF, LIBS and LA-ICP-MS, for the comparison of tape samples in different laboratories. In this study, the utility of X-Ray Fluorescence (XRF) is compared to previously published SEM-EDS and LA-ICP-MS data. Three XRF systems were used to evaluate a range of configurations commonly available at crime laboratories. A set of 40 electrical tape backings known to originate from difference sources was used to assess the inter-roll variability, discrimination and classification capabilities of the method. The discrimination for this tape set increased from 78.8% achieved by SEM-EDS to 81.5-91.0% by XRF, depending on the instrumental configuration. In comparison, LA-ICP-MS achieved 84.6% discrimination on these tapes. The overall characterization, classification, and discrimination capabilities improved with increasing sensitivity and selectivity of the methods SEM-EDS<XRF<LA-ICP-MS). A set of 20 pieces of tapes collected from the same roll were analyzed for intra-roll variability. Duplicate control same-source samples were used to evaluate inter-day and intra-day instrument variability. No false exclusions were observed in the data set, demonstrating the within-sample variability and instrumental variability are lower than the inter-sample variability. One concern of the method is the penetration depth of the X-beam beyond the target backing, requiring careful sample preparation to avoid interference from the adhesive or sample holder. XRF is a viable analytical tool for the forensic examination of electrical tapes, with advantages of speed of analysis, non-destruction of the tape, and high informing power. Two interlaboratory exercises were designed to study the performance of the different analytical methods for the forensic analysis of electrical tapes. The exercises were developed with the objective to imitate forensic case scenarios where known and question tapes are compared following the laboratory's analytical protocol. The participants were asked to compare the tape samples as in a regular forensic case. Seven (7) laboratories participated in the two interlaboratory exercises.

All the laboratories performing SEM-EDS in both interlaboratory exercises #1 and #2) were able to correctly associate the pairs of tapes originating from the same rolls, therefore the rate of false negatives was zero. Two of the laboratories performing SEM-EDS for the first interlaboratory exercise incorrectly associated two pairs of tapes belonging to different rolls, resulting in a 17% false positive rate. One of the laboratories performing SEM-EDS for interlaboratory exercise #2 incorrectly associated two pairs of tapes belonging in a 13% false positive rate. Up to 7 and 8 elements were detected by SEM-EDS for interlaboratory exercise #1 and #2, respectively. The increased sensitivity and selectivity of LIBS and LA-ICP-MS methods allowed to distinguish all the pairs of tapes originating from different sources and for correctly associate the tapes originating from the same rolls, resulting in no false positives or false negatives. In addition, increased characterization of the samples was obtained by detecting up to 14 elements by LIBS and 27 elements by LA-ICP-MS for interlaboratory exercise #2. A match criterion of ±5s allowed to numerically compare LIBS ratios and LA-ICP-MS signal areas for a more objective assessment of the differences between the tape samples.

Introduction

Adhesive tapes are occasionally received in forensic laboratories as substrates for different types of evidence such as DNA, fingerprints, fibers, and trace evidence. The tape itself, however, represents a very important type of evidence that can assist investigations in a variety of crimes that include the use of tapes in bindings, drug packaging, and the construction of improvised explosive devices, for example. The construction- and composition-related comparison of adhesive tapes in forensic laboratories consists typically of physical and microscopic examination followed by the analysis of the organic and inorganic components.

The physical and microscopic examination of tapes include the description of the texture of the backings, the color of the adhesive, the thickness of the different layers of the tapes, the number of different layers present, and when possible, the examination of potential physical fit between torn edges [1-8]. For most laboratories, visual examination is the first step of the analytical scheme and is usually followed by a supplemental instrumental method of analysis. The identification of the organic components of the tapes is usually accomplished by Infrared spectroscopy (IR) and Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC-MS) [5, 6, 8-12]. These two methods are almost orthogonal and therefore, when combined, provide improved characterization of the organic constituents and superior discrimination [6]. The inorganic analysis of tapes is commonly conducted by Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) and X-ray Fluorescence (XRF) [1, 2, 4-6, 8]. These techniques have proved useful in characterizing the elemental composition of tape samples. SEM-EDS has been shown to produce enhanced discrimination compared to physical examination, IR, and Py-GC-MS for the analysis of the backings of 90 electrical tapes [6]. Additional techniques have also been applied to this set of 90 tapes [13-15].

More recently, the methods of analysis incorporating Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) [16] and Laser Induced Breakdown Spectroscopy (LIBS) [17] have been developed for the chemical analysis of tape samples. These techniques have shown promising results for the analysis of tapes by increasing the number of elements detected, the confirmatory value of the results, and the sensitivity and selectivity of the analysis. The present work evaluates the informing power of the conventional methods physical examination, IR, Py-GC-MS, and SEM-EDS), and of LA-ICP-MS and LIBS for the analysis of electrical tapes by different laboratories.

Elemental analysis provides valuable information about the inorganic components present in tapes. These components are a part of the fillers, stabilizers, flame retardants, driers and other additives that are incorporated into tapes. The formulation of tapes varies significantly between manufactures and products and this information can be used in forensic examinations of tapes to characterize and classify tapes into groups of similar composition. Elemental profiling of tapes has been shown to be an informative analytical step that adds certainty to the conclusions derived from the complete examination and comparison of tape samples.

Two interlaboratory exercises were designed to study the performance of different analytical methods for the forensic analysis of electrical tapes. The exercises were developed with the objective to imitate forensic case scenarios where known (K) samples are compared to question Q) samples following the laboratory's analytical scheme. Seven laboratories participated in two interlaboratory exercises. The participants were asked to compare the tape samples as in a regular forensic case, using their standard protocol for the analysis of tapes.

Materials and Methods - Interlaboratory Exercises Design

Interlaboratory exercise #1 consisted of seven participant laboratories. Six samples of tapes: three known samples (K1, K2, and K3) and three questioned samples (Q1, Q2, and Q3) belonging to 3M Scotch and GE brands were sent out to the participant laboratories. There was a total of three pairs corresponding to the same rolls: K1 and Q2, K2 and Q3, and K3 and Q1 [31]. The identities of the samples were unknown to the participants. Four laboratories performed SEM-EDS analysis, three performed LIBS analysis, two performed LA-ICP-MS analysis. All laboratories performed physical/microscopic examination of the tapes and IR spectroscopy. Four laboratories performed Py-GC-MS to analyze the tape samples.

The results of interlaboratory #1 were discussed and evaluated among the participants before the design of interlaboratory exercise #2. The first interlaboratory exercise showed the potential of the elemental methods (mainly LIBS and LA-ICP-MS) to not only correctly distinguish the different pairs of tapes and associate the tapes from the same rolls, but also to increase the characterization of the samples by greatly expanding the number of detected elements. Interlaboratory exercise #2 was therefore focused on testing the performance of the different elemental techniques for the analysis of similar samples of tapes not previously distinguished by the organic analysis methods. The effect of different instrumental parameters in the performance of a specific technique was also evaluated.

Interlaboratory exercise #2 consisted of five participant laboratories performing only elemental methods of analysis (SEM-EDS, LIBS and LA-ICP-MS). To produce a more challenging set of samples, interlaboratory #2 consisted of four samples of tapes: a known sample (K1) and three questioned samples (Q1, Q2 and Q3) all belonging to the same brand (3M Scotch). The pairs K1 and Q2 originated from the same roll of tape (3M Scotch 700) [31]. The identities of the samples were unknown to the participants. These samples were selected from a set of tapes formerly analyzed by most of the techniques in question, and were not previously differentiated by physical and microscopic examination, IR spectroscopy, or Py-GC-MS [6, 16]. Four participant laboratories performed SEM-EDS analysis, five performed LIBS analysis, and three performed LA-ICP-MS analysis.

The participant laboratories provided their conclusions as to which pair of tapes could be distinguished and which ones were not differentiated. False positive and false negative error rates were estimated by documenting any disagreement between the anticipated conclusion e.g. known source of origin to be considered a true association or exclusion) and the conclusion reported by the participants based on their measured data. It is important to notice that the false positive and false negative rates were calculated for a small number of comparison pairs with the purpose of evaluating the performance of the different instrumental methods for this sample set. A larger set of comparison pairs is needed to fully assess Type I and Type II errors. In addition, the raw instrumental data from interlaboratory #2 was re-processed to compare the spectral data quantitatively using different match criteria: $\pm 3s$, $\pm 4s$ and $\pm 5s$.

Sample Set Description for Interlaboratory Exercise #1 and #2

The samples of tapes were prepared by selecting a section (-20 cm) of the tape rolls and attaching them to a plastic substrate Apollo Plain Paper Copier Transparency Film . The individual samples consisted of six (-2 cm by -2 cm) pieces of tapes labeled as K1, K2, K3, Q1, Q2, and Q3 for interlaboratory exercise #1 and K1, Q1, Q2 and Q3 for interlaboratory exercise #2. The sample description for all samples in both interlaboratory exercises is given in [31]. Each laboratory was asked to compare the known sample to all the questioned sample, for a total of nine comparison pairs for interlaboratory exercise #1, and three comparison pairs for interlaboratory exercise #2.

Samples for interlaboratory exercise #1 were selected to include three different situations: two tape samples originating from a same roll that should be indistinguishable, two different tape samples of the same brand that may be differentiated by some of the most selective and sensitive methods, and two different samples from different brands that should be distinguishable by most techniques.

Samples for interlaboratory exercise #2 were selected to include tape fragments originating from the same tape roll, and tape samples from the same brand which could not be distinguished by physical examination or IR spectroscopy, but that showed differences in their elemental composition. The purpose of interlaboratory exercise #2 was to evaluate the performance of the different elemental techniques for the comparison of similar tapes from the same brand. Instrumental Parameters

Participants were asked to compare each known and question sample by their available methodology. For the participants without a protocol for the specific instrumentation, a set of parameters were suggested for the analysis of tapes by such a technique, based on previous studies [6, 16]. The participant laboratories were asked to provide detailed description of the parameters used for the elemental analysis techniques; this would allow to estimate the effect of some parameters in the sensitivity and selectivity of the method.

The analytical and instrumental parameters for the different instrumentation (SEM/EDS, LIBS and LA-ICP-MS) were optimized to obtain the best signal to noise ratio SNR) and smallest relative standard deviation (%RSD) are reported in references 16 and 31 for each of the participating laboratories.

Data Pre-Processing

The data collected for SEM-EDS was in the form of energy spectra (counts vs. x-ray energy). Data preprocessing included background subtraction and estimation of SNR as reported by Ernst et al. [18]. All the emission lines selected for LIBS were confirmed by the presence, and abundance, of two or more emission lines for each element. The emission lines selected were those with no known interferences, smaller %RSD, and larger SNR. Integration of the area under selected peaks of the elements of interest followed by the ratio of the elements was applied to the data used for numerical comparison. The element lines selected for LIBS match criteria comparison were the following: Sb 259.8 nm, Si 288.2 nm, Ti 334.9 nm, Mo 386.4 nm, C 247.8 nm, Ca 393.4 nm, Al 396.2 nm, Cr 427.5 nm, Cd 480.0 nm, Zn 481.1 nm, Pb 405.8 nm, Sr 407.8 nm, Mg 518.4 nm, Na 589.0 nm, Ba 614.2 nm, Li 670.8 nm, K 766.5 nm. These elements were determined to be present if the SNR>3.

The data collected for LA-ICP-MS was in the form of mass scan intensity counts vs. mass-to-charge ratio) and transient mode (intensity counts vs. time .

LA-ICP-MS spectra in mass scan mode were especially useful for spectral overlay comparison. Data preprocessing for LA-ICP-MS for spectral overlay included the removal of non-relevant mass-to-charge peaks originating from polyatomic and isobaric interferences [19] and normalization to the sum of the intensity peaks as a mean to compensate for any shot-to-shot variation and inter-day variations [16]. In the absence of an internal standard, this normalization strategy accounts for small differences in the ablated mass between samples and improves both repeatability and reproducibility of each individual sample [16]. All the isotopes selected for LA-ICP-MS were confirmed by their isotopic pattern and natural abundance.

LA-ICP-MS data collected in transient mode (intensity vs. time) is not suitable for spectral overlay comparison. Instead, the GeoPRO (CETAC Technologies, v 1.0, NE) software was used to integrate the area under the curve for the selected isotopes for further statistical analysis using different match criteria. The elements were determined to be present if the SNR>3. The isotopes selected were those with larger abundance and no known interferences. The isotopes used for LA-ICP-MS match criteria comparison are the following: ²⁷Al, ^{135, 137}Ba, ¹³C, ^{42, 44}Ca, ¹¹¹Cd, ³⁵Cl, ⁵⁷Fe, ³⁹K, ¹³⁹La, ⁷Li, ^{24, 26}Mg, ²³Na, ^{206, 208}Pb ^{121, 123}Sb,

^{28, 29}Si, ^{118, 119}Sn, ^{86, 88}Sr, ^{47, 48}Ti, ²³²Th ^{64, 66}Zn, ^{90, 91}Zr.

Comparison Criteria

Physical and microscopic examination comparison criteria varied greatly between laboratory. Most laboratories compared tapes based on the thickness of the backing and/or adhesive layer and the appearance of both backing and adhesive.

The laboratories comparing backing texture determined that tapes were distinguishable based on the shiny or matte finish, and on dimples or marks on the surface. Physical examination and microscopy were, however, followed by a more discriminating technique (IR, Py-GC-MS, SEM-EDS, LIBS, or LA-ICP-MS).

IR comparisons were performed by spectral overlay between the samples. The samples were differentiated by the presence or absence of peaks in the overlay comparison. In some cases, these peaks were attributed to adipates or phthalates present in the tapes.

Py-GC-MS samples were differentiated by the retention time, fragmentation pattern, and confirmation of the presence of specific organic components using the different fragmentation patterns. The identified organic components were present in some tapes and not others, therefore allowing to differentiate the tape pairs originating from different sources.

SEM-EDS, LIBS and LA-ICP-MS comparisons were performed by spectral overlay. The spectral overlay comparisons account for variability within replicate measurements, which includes instrumental variations and compositional variations in the sampled locations. Two samples were differentiated if the variation of the spectral peaks of the replicates of the questioned item did not fall within the observed range of variation of the respective spectral peaks of the replicates of the known sample. The variability was documented for the x-axis of the analyte peaks (e.g., identification of elements by energy, wavelength or m/z) and for the y-axis (e.g., counts, peak intensity or area correlated with the concentration of each element in the samples). Two samples were differentiated if at least one element fell outside the spectral overlay criteria.

In the case of LIBS comparisons, the presence and abundance of two or more emission lines for the element in question confirmed its presence in the samples. For LA-ICP-MS, relative natural abundance of different isotopes was used to confirm the identification of each element.

In addition to spectral overlay comparisons, different match criteria were tested for the numerical comparison of tapes for LIBS and LA-ICP-MS. Although spectral overlay provides a visual comparison of the samples and allows for the identification of the element menu in the samples, it can be subjective when samples are very similar to each other. Spectral overlay is also time consuming when the sample comparison set is large.

In efforts to numerically compare the elements in the samples for LIBS and LA-ICP-MS, different match criteria were studied: ± 3 s, ± 4 s and ± 5 s, where s represents the standard deviation of the known sample. If the mean of at least one element or ratio in the sample in question falls outside the range of the mean and standard deviation of the known sample, the two tapes are said to be distinguished from each other by the measured properties. If all elements in the question sample fall within the range of standard deviation of the known sample, the two tapes are indistinguishable from each other.

To perform the different match criteria for all laboratories, the data was processed in the same manner for all laboratories and the selected elements or ratios were those detected by the laboratories in at least one sample.

The best match criterion for LIBS and LA-ICP-MS was found to be the $\pm 5s$ interval. This match criterion resulted in the correct association of the tapes belonging to the same rolls and differentiation of the tapes from different rolls, resulting in zero type I and type II errors.

In the case of LIBS comparisons, the match criteria were applied to the ratios of the peak areas. LIBS variability between replicate measurements, as well as the effect of the sample matrix in the resulting spectra can be minimized using ratios. This method works on the premise that ratios between different elements should remain relatively constant, regardless of the matrix composition and instrumental variations.

Results and Discussion -- Interlaboratory Exercise #1 Results Scanning Electron Microscopy Energy Dispersive Spectroscopy (SEM-EDS)

All the laboratories performing SEM-EDS in interlaboratory #1 were able to correctly associate K1 to Q2 (3M Scotch Super 88, USA), K2 to Q3 GE, Taiwan), and K3 to Q1 (3M Scotch 700, USA), therefore the rate of false negatives was zero; these pairs of tapes belong to the same rolls and based on predistribution analysis were expected to be indistinguishable [31]. However, laboratories C and D were not able to detect enough differences between the different models of 3M Scotch tapes (K1 vs. Q1, and K3 vs. Q2). In the case of K2 (GE, made in Taiwan), this tape was always correctly distinguished from the 3M Scotch tapes based on its elemental profile.

The total number of comparison pairs for interlaboratory exercise #1 was 9 for a total of 4 participating laboratories. From these 36 comparison pairs, 12 correspond to same roll comparisons, and 24 correspond to different roll comparisons. Two of the laboratories performing SEM-EDS incorrectly associated two pairs of tapes belonging to different rolls, therefore 4 comparison pairs contributed to a 17% false positive rate (4 undistinguished pairs out of 24 comparison pairs) 2). These false positive and false negative rates were calculated for a small number of comparison pairs to evaluate the performance of the different instrumental methods for these specific samples. Ideally, a larger set of comparison pairs is needed to fully assess Type I and II error rates.

_	Method	Exercise #1		Exercise #2	
		FPR (%)	FNR (%)	FPR (%)	FNR (%)
	SEM-EDS	17 (4 out of 24)	0	13 (1 out of 8)	0
	LIBS	0	0	0	0
	LA-ICP-MS	0	0	0	0

Table 1: False positive rate (FPR) and false negative rate for the elemental techniques in interlaboratory exercises.

Figure 1 shows the SEM-EDS spectral overlay comparison for Lab D for K1, Q1, Q2, and Q3. Sample K1 was differentiated from sample Q3 based on the higher amounts of Al 1.486 Ka) and Si 1.740 Ka) present in Q3. Sample K1 was not distinguished from Q1 and Q2 using SEM-EDS by laboratory D.

In contrast, Lab A was able to differentiate the 3M Scotch tapes (Super 88 and 700). Figure 2 shows the SEM-EDS spectral overlay comparison of K1, Q1, Q2, and Q3 by Lab A for interlaboratory exercise #1. Sample K1 was differentiated from Q3 based on the presence of a shoulder next to the largest Sb 3.606 La) peak, due to the higher amounts of Ca (3.691 Ka) in K1 and Q2. This difference in Ca (3.691 Ka) was detected by Lab C and Lab D, but not considered enough for an exclusion due to the lack of resolution among the Ca and Sb peaks and the relatively low SNR of the signal. It is worth noting that the SNR for the Sb La /Ca Ka peak observed by laboratories C and D was at least one order of magnitude lower than

the respective SNR observed by laboratories A and B, indicating that the sensitivity of the SEM-EDS instruments is highly dependent on instrumental configurations and operating conditions.

The relatively lower sensitivity of instrumental configurations C and D in comparison to those of laboratories A and B is also reflected in the overall element menu detected by SEM-EDS for the participant laboratories [31]. Although the laboratories selected up to 4-7 elements by SEM-EDS, only Ca appeared to differentiate the 3M Scotch tapes for laboratories A and B. One factor that contributed in the discrepancy of calcium content is the relatively low selectivity and sensitivity observed by the Ca Ka peak. Laboratories C and D did not differentiate the pair K1 and Q1 based on just the wider signal around the 3.4 keV area (Figure 2); this difference between the samples was not considered large enough to constitute an exclusion. In the case of the GE tape, all laboratories differentiated this tape from the 3M Scotch tapes based on Al and Si.

Laser Induced Breakdown Spectroscopy (LIBS)

The pairs of tapes belonging to the same rolls: K1 and Q2 (3M Scotch Super 88, USA), K2 and Q3 GE, Taiwan), and K3 and Q1 3M Scotch 700, USA) were all correctly associated by LIBS analysis in interlaboratory exercise #1. All the laboratories correctly differentiated the two different 3M Scotch tape pairs (K1 vs. Q1 and K3 vs. Q2) [31]. In contrast with SEM-EDS, Ca was easily detected by LIBS (Figure 3) for all labs. Moreover, LIBS detected the same elements identified by SEM-EDS with the addition of C, Ba, K, Li, Na, Mo, Si, Sr, and Ti.

Figure 3 shows the LIBS spectral overlay comparison for samples K1, Q1, Q2, and Q3 for laboratory A. Sample K1 was differentiated from Q1 based on the higher amounts of Mo and Ca in sample K1. Also, K1 was differentiated from Q3 based on Ba, Ca and Ti. Additionally, the three pairs of tapes originated from the same roll were correctly associated and the element menu detected is reported in [31]. The main differences between the two 3M Scotch tapes (Super 88 and 700) consist of the higher amounts of Mo and Ca in K1 and Q2 (3M Scotch Super 88). These differences in Ca were not always resolved from the Sb peaks by SEM-EDS due to lower selectivity of the technique. In the same manner, Mo and Zn were not always detected in SEM-EDS due to the lower sensitivity of the technique compared to LIBS. The Super 88 electrical tape is of a higher quality compared to the commercial grade 3M Scotch 700, therefore some extra components might have been added to the formulation to improve its performance. A review of several electrical tape and pressure sensitive adhesives patents [20-25] confirmed the use of calcium carbonate and calcium sulfate, as well as zinc oxides and silicates and inorganic fillers. Similarly, molybdenum oxide is known to be a flame retardant added to the formulation of tapes. Due to the higher sensitivity and selectivity of LIBS, more elements were detected per sample and this allowed further discrimination of the similar 3M tapes that belong to different rolls K1 vs. Q1 and K3 vs. Q2), which were not always distinguished by SEM-EDS. The rate of false negatives and false positives for LIBS was found to be zero (see Table) as LIBS allowed the correct association of all tapes belonging to the same rolls and differentiation of the tapes from different rolls in this study.

Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS)

All the laboratories performing LA-ICP-MS were able to correctly associate pairs of tapes belonging to the same rolls which were expected to be indistinguishable [31]. The 3M Scotch tapes belonging to different rolls (K1 vs. Q2 and K3 vs. Q2) were correctly differentiated by LA-ICP-MS analysis as well. The element menu obtained by LA-ICP-MS for interlaboratory exercise #1 for each pair of tapes is reported in [31]. The element menu obtained by LA-ICP-MS increased compared to LIBS by the addition of Ce, Co, Cu, Cl, Fe,

La, Mn, Nb, Nd, Ni, Pr, Sn, W, and Y. These elements are present in the tapes at concentrations below the limits of detection of LIBS but could be detected by LA-ICP-MS due to the improved sensitivity and selectivity of this method. The rate of false positives and false negatives for LA-ICP-MS comparisons were found to be zero for this data set (Table 1). It is important to note that LIBS was especially useful in detecting Li, which is a very difficult element to detect in LA-ICP-MS. Li can be difficult to detect in LA-ICP-MS due to space-charge effects between light and heavy ions in the mass spectrometer [26]. Lithium is a good emitter, easily detected by LIBS in most samples at very low concentrations. In the same manner, calcium and potassium, which are known to present interferences with Ar in ICP-MS, are easily detected by LIBS and confirmed by multiple lines throughout the spectra.

Figure 4 shows the LA-ICP-MS spectral overlay comparison between K1, Q1, Q2, and Q3 for laboratory B for interlaboratory exercise #1. K1 was differentiated from Q1 based on the higher amounts of Sr and Sn in K1. K1 and Q3 were differentiated based on the higher amounts of Ti in Q3, and the higher amounts Mo, Sr and Sn in K1. K1 and Q2 were not distinguished by LA-ICP-MS based on spectral overlay comparisons; this pair of tapes belong to the same roll. Interlaboratory #1 showed the potential of the elemental methods (mainly LIBS and LA-ICP-MS) to not only correctly distinguish the different pairs of tapes and associate the tapes from the same rolls, but also to increase the characterization of the samples by detecting up to 14 elements by LIBS and 20 elements by LA-ICP-MS.

Additional Techniques

Additional techniques including physical examination, Infrared Analysis and Pyrolysis GC-MS were performed as part of the interlaboratory exercises by the participant laboratories. The results for each of the laboratories for all of these additional techniques is reported in [31]. SEM-EDS produced the best discrimination power compared to physical examination, IR, and Py-GC-MS for the analysis of the backings of 90 electrical tapes [6]. LIBS and LA-ICP-MS show the potential for even better discrimination than all of these techniques combined.

Interlaboratory Exercise #2 Results

In order to produce a more challenging set of samples, interlaboratory #2 consisted of four tapes: a known sample (K) and three questioned samples (Q) all belonging to the same brand (3M Scotch), but from different rolls [31. The pairs K1 and Q2 belong to the same roll of tape (3M Scotch 700). These samples were selected from a set of tapes that was previously analyzed by most of the techniques in question, and were not previously differentiated by physical and microscopic examination, IR spectroscopy, or Py-GC-MS, but were differentiated by LA-ICP-MS [6, 16]. Four participant laboratories performed SEM-EDS analysis, five performed LIBS analysis, and three performed LA-ICP-MS analysis.

SEM-EDS

The four laboratories performing SEM-EDS compared the samples by spectral overlay. The spectral overlay by SEM-EDS for Lab B for interlaboratory exercise #2 is reported in [31]. Sample K1 was differentiated from sample Q1 based on the higher amounts of Mg 1.254 Ka) in K1, and P (2.013 Ka), Pb (2.342 Ma) and Ca 3.69 Ka) present in Q1. Sample K1 was distinguished from Q3 for based on the Ca (3.691 Ka) shoulder on the Sb (3.604 La) peak. K1 was not distinguished from Q2 by SEM-EDS; K1 and Q2 belong to the same tape roll [31]. In the case of Laboratory D, the difference in the Ca shoulder between the signals was reported as inconclusive and not enough to differentiate the two samples for the same issues of selectivity and sensitivity discussed for the first exercise. The total number of comparison pairs for interlaboratory exercise #2 was 3 [31] for a total of 4 participating laboratories. From these 12 comparison pairs, 4 correspond to same roll comparisons, and 8 correspond to different roll comparisons. One of the

laboratories performing SEM-EDS incorrectly associated two pairs of tapes belonging to different rolls, therefore 1 comparison pair contributed to a 13% false positive rate (1 undistinguished pair out of 8 comparison pairs) (Table 1). This false positive rate was calculated for a small number of comparison pairs with the purpose of evaluating the performance of the different instrumental methods for this small sample set. To fully assess Type I and II errors, a larger sample set would be ideal.

LIBS

All the tape samples belonging to different rolls K1 vs. Q1, and K1 vs. Q3) were correctly differentiated by LIBS analysis for interlaboratory #2. The samples K1 to Q2, which belong to the same roll, were always correctly associated by LIBS.

Figure 5 shows the spectral overlay comparison of K1 vs. Q1, Q2, and Q3 for Lab C for Interlaboratory exercise #2 for Ca and Ba lines. Sample K1 was differentiated from Q1 and Q3 based on the higher amounts of Ca and Ba in K1. Samples K1 and Q2 were indistinguishable for all the elements examined, these samples belong to the same tape roll (Table 1).

All laboratories performing LIBS analysis compared the samples by spectral overlay. Some laboratories further compared the samples using $\pm 3s$, $\pm 4s$ and $\pm 5s$ match criteria for the peak area and peak ratios comparisons.

The element lines and ratios selected varied greatly between laboratories. To further study the best match criterion, the data obtained from the five different laboratories was re-processed and analyzed in the same manner for all laboratories and the results for all labs is reported in [31].

Using the proposed match criterion for the comparison of ratios, four out of the five laboratories correctly associated samples K1 and Q2 which belong to the same roll of tape. In the case of laboratory D, the two tapes originating from the same roll were distinguished based on the Na/Mg ratio. Sodium has been found to be detected in tapes due to handling contamination sweat), which might have caused the false exclusion between K1 and Q2. If Na is removed from the element menu before ratio analysis, the two samples are indistinguishable from each other. This emphasizes the importance of selecting a representative element menu that explains the variations between samples due to the manufacturing process of different tapes, and not due to contamination interferences. This match criterion allowed for the correct discrimination of the tape samples belonging to different rolls K1 vs. Q1, and K1 vs. Q3). The element menu obtained by each laboratory for LIBS is shown in [31]. The elements detected were those with a SNR>3.

LA-ICP-MS

All the laboratories performing LA-ICP-MS correctly differentiated the tape samples from different rolls (K1 vs. Q1, and K1 vs. Q3). All laboratories correctly associated K1 to Q2, which belong to the same roll.

Figure 6 shows the LA-ICP-MS spectral overlay comparison for Lab B for interlaboratory exercise #2 using the mass scan mode. Sample K1 was differentiated from Q1 based on their differences in Mo, Sr, Cd, Sn, Cu, and Zn. K1 was distinguished from Q3 based on Mo, Nb, Sr, Cd, Sn, and Cu. K1 and Q2 were not distinguished by LA-ICP-MS, both belong to the same tape roll. The element menu detected (SNR>3) by LA-ICP-MS for interlaboratory exercise #2 for each laboratory is summarized in [31]. Using the proposed match criterion \pm 5s) for the comparison of integrated signal, all the laboratories performing LA-ICP-MS correctly associated samples K1 and Q2. This method also correctly discriminated the tape samples belonging to different rolls. Match criteria comparisons allowed to objectively compared two samples and allowed for reporting the elements that produced the highest variability between sample pairs. This method can be automated to facilitate the comparison between several sample pairs without the need of performing

one-to-one spectral overlay comparisons. LA-ICP-MS analysis detected most of the elements identified by LIBS with the addition of Cl, Co, Cu, Fe, La, Mn, Nb, Nd, Ni, Pr, Rb, Sb, Sn, Sr, Tl, W, Y, Zn and Zr, which were not detected by LIBS due to the lower sensitivity of this method. Similarly to interlaboratory #1, LIBS proved useful in detecting problematic elements for LA-ICP-MS such as Li, Ca, and K.

Conclusions

Two interlaboratory exercises were designed to study the performance of different analytical methods for the forensic analysis of electrical tapes. The exercises simulated forensic case scenarios where known K) samples are compared to question (Q) samples following the laboratory's analytical scheme. Two of the laboratories performing SEM-EDS for the first interlaboratory exercise incorrectly associated two pairs of tapes belonging to different rolls, therefore resulting in a 17% false positive rate. One of the laboratories performing SEM-EDS for interlaboratory exercise #2 incorrectly associated two pairs of tapes belonging to different rolls, resulting in a 13% false positive rate. These false inclusions were the result of the lower selectivity of the method which prevented detecting differences in calcium and antimony for selected samples, as well as the lower sensitivity of the technique which prevented the detection of elements present in tapes below SEM-EDS detection limits. It is important to clarify that these false positive and false negative rates were calculated for a small number of comparison pairs with the purpose of evaluating the performance of the different instrumental methods for this sample set. A larger set of comparison pairs is needed to fully assess Type I and Type II errors. Up to 7 and 8 elements were detected by SEM-EDS for interlaboratory exercise #1 and #2, respectively. Elemental analysis of electrical tape backings provided valuable information about the inorganic components added to the formulation of tapes. The increased sensitivity and selectivity of LIBS and LA-ICP-MS methods allowed to always distinguish the pairs of tapes originating from different sources, to correctly associate the tapes belonging to the same rolls, and to increase the characterization of the samples by detecting up to 14 elements by LIBS and 27 elements by LA-ICP-MS for interlaboratory exercise #1, and 17 elements by LIBS and 32 elements by LA-ICP-MS for interlaboratory exercise #2. Elemental analysis alone seems to have informative capability similar to combined organic analytical tools (i.e. IR and Py-GC-MS) with the advantage that analyses are less destructive and faster than Py-GC-MS, therefore it may be used as a fast screening step early in the analytical protocol to reduce backlog. A match criterion of $\pm 5s$ allowed to objectively compare LIBS ratios and LA-ICP-MS signal areas. This method proved useful in providing an automated way to show the elements/ratios responsible for the distinction of tapes originating from different sources, as well as confirmation of the level of association for tape samples originating from the same roll. The informing power, discrimination capabilities, classification potential, and certainty in the identification of elemental components increased with superior sensitivity and selectivity of the methods in the following order SEM-EDS < LIBS < LA-ICP-MS. Standardized methods currently exist for SEM-EDS, IR and Py-GC-MS. [28-30] This study is a first effort towards standardization of the LA-ICP-MS and LIBS analytical and comparison methods [31]. The results show there is good analytical agreement among the participating laboratories. Further developments in the standardization of methods for comparison of spectrochemical data will improve the overall forensic utility of the methods described. Further research is required in order to compare the results from different laboratories to each other. A quantitative method of analysis would allow for a comparison of the data from different labs, regardless of the instrumental parameters used. In addition, if a standardized method of analysis is applied, ratios of elements would facilitate the comparison between different laboratories for a single technique.

Appendix 1:

The following manuscripts have been published as a result of this research project:

- 1. Anjali Gupta, Claudia Martinez-Lopez, James M. Curran and Jose R. Almirall, Multi-element Comparisons of Tapes Evidence using Dimensionality Reduction for Calculating Likelihood Ratios, *Forensic Science International*, 2019, accepted for publication June 3, 2019.
- 2. Meghan Prusinowski, Andria Mehltretter, Claudia Martinez-Lopez, Jose Almirall, Tatiana Trejos, Assessment of the utility of X-ray Fluorescence for the chemical characterization and comparison of black electrical tape backings, *Forensic Chem.*, 2019, 13, 100-146. https://doi.org/10.1016/j.forc.2019.100146
- 3. C Martinez-Lopez, T Trejos, S Coulson, C Pollock and JR Almirall, An Inter-laboratory Evaluation of Elemental Analysis of Adhesive Tapes, *Forensic Chemistry*, 2019 (12) 66-77. https://doi.org/10.1016/j.forc.2019.01.001
- 4. C Martinez-Lopez, M Sakayanagi, and JR Almirall, Elemental analysis of packaging tapes by LA-ICP-MS and LIBS, *Forensic Chemistry*, 2018, (8), 40-48. <u>https://doi.org/10.1016/j.forc.2017.03.003</u>
- 5. C Martinez-Lopez, T Trejos, AH Mehltretter and **JR Almirall**, Elemental analysis and characterization of electrical tape backings by LA-ICP-MS, *Forensic Chemistry*, **2017**, (4), 96-107. <u>http://dx.doi.org/10.1016/j.forc.2017.03.003</u>

Appendix 2: Figures 1-6



Figure 1: SEM-EDS spectral overlay comparison of K1 vs. Q1, Q2, and Q3 for Lab D for interlaboratory exercise #1. Sample K1 was differentiated from sample Q3 based on the higher amounts of A1 (1.486 Ka) and Si (1.740 Ka) present in Q3. Sample K1 was not distinguished from Q1 and Q2 by SEM-EDS by this laboratory.



Figure 2: SEM-EDS spectral overlay comparison of K1 vs. Q1, Q2, and Q3 for Lab A for interlaboratory exercise #1. Sample K1 was differentiated from Q2 based on the presence of Ca (3.691 Ka) in K1 and Q2.



Figure : LIBS spectral overlay comparison of K1 vs. Q1, Q2, and Q3 for Lab A for exercise #1. Sample K1 was differentiated from Q1 based on the higher amounts of Mo and Ca in sample K1. K1 was differentiated from Q3 based on Ba, Ca and Ti.



Figure 4: LA-ICP-MS spectral overlay comparison of K1 vs. Q1, Q2, and Q3 for Lab B for exercise #1. K1 was differentiated from Q3 based on Ti, Mo, Sr, and Sn. Sample K1 was differentiated from Q1 based on Mo, Sr, and Sn.



Figure 5: LIBS spectral overlay comparison of K1 vs. Q1, Q2, and Q3 for Lab C for interlaboratory exercise #2. Sample K1 was differentiated from Q1 and Q3 based on the higher amounts of Ca and Ba in K1.



Figure 6: LA-ICP-MS spectral overlay comparison of K1 vs. Q1, Q2, and Q3 for Lab B for interlaboratory exercise #2. Sample K1 was differentiated from Q1 based on their differences in Mo, Sr, Cd, Sn, Cu, and Zn. K1 was distinguished from Q3 based on differences in Mo, Nb, Sr, Cd, Sn, and Cu.

References

- 1. Keto, R.O. Forensic characterization of black polyvinyl chloride electrical tape. in Proceedings of the International Symposium on the Analysis and Identification of Polymers. 1984.
- 2. Kee, T.G. The characterization of PVC adhesive tape. in Proceedings of the International Symposium on the Analysis and Identification of Polymers. 1984.
- 3. Blackledge, R., *Tapes with adhesive backings: Their characterization in the forensic science laboratory.* 1987, Carl Hanser Verlag, Munich. p. 413-421.
- 4. Goodpaster, J.V., et al., *Identification and comparison of electrical tapes using instrumental and statistical techniques: I. Microscopic surface texture and elemental composition.* Journal of Forensic Sciences, 2007. **52** 3): p. 610-629.
- 5. Mehltretter, A.H., M.J. Bradley, and D.M. Wright, *Analysis and Discrimination of Electrical Tapes: Part I. Adhesives.* Journal of Forensic Sciences, 2011. **56** 1): p. 82-94.
- 6. Mehltretter, A.H., M.J. Bradley, and D.M. Wright, *Analysis and Discrimination of Electrical Tapes: Part II. Backings.* Journal of Forensic Sciences, 2011. **56**(6): p. 1493-1504.
- 7. Bradley, M.J., et al., *A validation study for vinyl electrical tape end matches*. Journal of Forensic Sciences, 2011. **56** 3): p. 606-611.
- 8. Wright, D.M. and A.H. Mehltretter, *Duct Tape Sourcing Examinations: Developing Investigative Leads using Multiple Resources.* Journal of the American Society of Trace Evidence Examiners, 2013. **4** 1): p. 13-28.
- 9. Williams, E.R. and T.O. Munson, *The comparison of black polyvinylchloride (PVC) tapes by pyrolysis gas chromatography.* Journal of Forensic Sciences, 1988. (5): p. 1163-1170.
- Merrill, R.A. and Edward G. Bartick, Analysis of Pressure Sensitive Adhesive Tape: I. Evaluation of Infrared ATR Accessory Advances. Journal of Forensic Sciences, 2000. 45 1): p. 93-98.
- 11. Goodpaster, J.V., et al., *Identification and comparison of electrical tapes using instrumental and statistical techniques: II. Organic composition of the tape backing and adhesive.* Journal of Forensic Sciences, 2009. **54** 2): p. 328-338.
- 12. Zieba-Palus, J., et al., *Pyrolysis-gas chromatography/mass spectrometry analysis as a useful tool in forensic examination of automotive paint traces.* Journal of Chromatography A, 2008. **1179** 1): p. 41-46.
- *13.* Dietz, M.E., et al., *Forensic utility of carbon isotope ratio variations in PVC tape backings.* Science & Justice, 2012. **52** 1): p. 25-32.
- Henning, S., T. Schonberger, and U. Simmross, *The Pabst's method: An effective and low-budget tool for the forensic comparison of opaque thermoplastics-Part 1: Additional discrimination of black electrical tapes.* Journal of Forensic Science International, 2013.
 2 1-3): p. 387-392.
- 15. Schoenberger, T., U. Simmross, and C. Poppe, *Forensic examination of electrical tapes using high resolution magic angle spinning 1 H NMR spectroscopy*. Journal of Analytical and Bioanalytical Chemistry, 2016. **408** 1): p. 123-129.

- 16. Martinez-Lopez, C., et al., *Elemental analysis and characterization of electrical tape backings by LA-ICP-MS.* Forensic Chemistry, 2017: p. 96-107.
- 17. Martinez-Lopez, C., M. Sakayanagi, and J.R. Almirall, *Elemental analysis of packaging tapes by LA-ICP-MS and LIBS*. Forensic Chemistry, 2018. **8**: p. 40-48.
- 18. Ernst, T., et al., Signal-to-noise ratios in forensic glass analysis by micro X-ray fluorescence spectrometry. X-Ray Spectrometry, 2014. 4 1): p. 13-21.
- 19. Trejos, T., et al., *Characterization of toners and inkjets by laser ablation spectrochemical methods and Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy*. Spectrochimica Acta Part B: Atomic Spectroscopy, 2014. **92**: p. 9-22.
- 20. Oace, R.J., S.R. Burns, and E.E. Eastwold, U.S. 2559990A. Insulating tape. 1946, Minnesota Mining & Mfg.
- 21. Hofmann, C.F., C.H. Vondracek, and D.C. Westervelt, *U.S. 3082133A. High temperature electrical insulating tape.* 1957, Westinghouse Electric Corp.
- 22. Barton, D.M., US3162722 Electric Tape Insulation. 1964, Dow Corning Corporation: United States.
- 23. Miller, J.A., *Pressure Sensitive Adhesive Composition*. 1970, Morgan Adhesives Company.
- 24. Blance, R.B. and D.M. Gardner, *US3632412 Electrical Tape*. 1972, Monsanto Company: United States.
- 25. Garcia-Ramirez, R., D.V. Mahoney, and S.O. Ward, *W.O. 2002018507A1. Solventless plasticizer-resistant vinyl electrical tape.* 2002, 3M Innovative Properties Co.
- 26. Taylor, H.E., *Inductively Coupled Plasma-Mass Spectrometry: Practices and Techniques*. 2000: Academic Press.
- Smith, J.M., Forensic examination of pressure sensitive tape, in Forensic Analysis on the Cutting Edge: New Methods for Trace Evidence Analysis, R.D. Blackledge, Editor. 2007. p. 291-332.
- 28. Guideline for Using Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy in Forensic Tape Examinations: Scientific Working Group on Materials Analysis (SWGMAT). Journal of the American Society of Trace Evidence Examiners, 2011. **2**(1): p. 122-132.
- 29. Guideline for Using Fourier Transform Infrared Spectroscopy in Forensic Tape Examinations: Scientific Working Group on Materials Analysis (SWGMAT). Journal of the American Society of Trace Evidence Examiners, 2011. **2** 1): p. 112-121.
- 30. Standard Guide for Using Pyrolysis Gas Chromatography and Pyrolysis Gas Chromatography/Mass Spectrometry in Forensic Tape Examinations: Scientific Working Group on Materials Analysis (SWGMAT). Journal of the American Society of Trace Evidence Examiners, 2014. **5** 1): p. 42-50.
- 31. <u>C Martinez-Lopez</u>, T Trejos, S Coulson, J Goodpaster, K Igowsky, F Kuczelinis, A Mehltretter, E Pollock, U Simmross, R Weimer, P Weis, JR Almirall, Interlaboratory Evaluations of the Performance of Elemental Analytical Methods for the Forensic Analysis and Comparisons of Electrical Tapes, *For. Chem.*, 2019 12) 66-77.