

Interlaboratory Evaluations of the Performance of Elemental Analytical Methods for the Forensic Analysis and Comparisons of Electrical Tapes

Claudia Martinez-Lopez^a, Tatiana Trejos^b, Sally Coulson^c, John Goodpaster^d, Katherine Igowsky^e, Felix Kuczelinis^f, Andria Mehlretter^g, Edward Pollock^h, Ulrich Simmross^f, Robyn Weimerⁱ, Peter Weis^f, Jose R. Almirall^{a*}

^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

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 evidence such as drug packaging. The 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.

This work 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, LIBS and LA-ICP-MS, for the comparison of tape samples in different laboratories.

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 to different rolls, resulting 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 #1, and 17 elements by LIBS and 32 elements by LA-ICP-MS for interlaboratory exercise #2. A match criterion of $\pm 5s$ 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 including the use of isotope ratio mass spectrometry [13-16].

More recently, the methods of analysis incorporating Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) [17] and Laser Induced Breakdown Spectroscopy (LIBS) [18] 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 (Table 1). 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) (Table 1). 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 note 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. Table 1 shows the sample description for both interlaboratory exercises. 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.

Table 1: Sample pairs description and expected results for interlaboratory exercise #1 and #2.

Exercise	Comparison Pair	Sample Origin	Expected Results
1	K1 vs. Q1	Same brand, different model (3M Scotch Super 88/3M Scotch 700)	Different elemental composition
	K1 vs. Q2	Same brand, same model, same roll (3M Scotch Super 88, made in USA)	Same elemental composition
	K1 vs. Q3	Different brand, different model (3M Scotch Super 88/GE)	Different elemental composition
	K2 vs. Q1	Different brand, different model (GE/3M Scotch 700)	Different elemental composition
	K2 vs. Q2	Different brand, different model (GE/3M Scotch Super 88)	Different elemental composition
	K2 vs. Q3	Same brand, same model, same roll (GE, made in Taiwan)	Same elemental composition
	K3 vs. Q1	Same brand, same model, same roll (3M Scotch 700, made in USA)	Same elemental composition
	K3 vs. Q2	Same brand, different model (3M Scotch 700/3M Scotch Super 88)	Different elemental composition
	K3 vs. Q3	Different brand, different model (3M Scotch 700/GE)	Different elemental composition
2	K1 vs. Q1	Same brand, different model (3M Scotch 700/3M Scotch Super 33+, made in USA)	Different elemental composition
	K1 vs. Q2	Same brand, same model, same roll (3M Scotch Super 700, made in USA)	Same elemental composition
	K1 vs. Q3	Same brand, same model, different roll (3M Scotch Super 33+, made in USA)	Different elemental composition

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 questioned 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, 17]. 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. Table 2, Table 3, and Table 4 show the parameters for SEM-EDS, LIBS and LA-ICP-MS, respectively. The instrumental parameters for the different instrumentation were optimized to obtain the best signal to noise ratio (SNR) and smallest relative standard deviation (%RSD). The identification code (A, B, C, ...) for the laboratories was randomly assigned for each individual technique; this identification code was also rotated among analytical methods so that lab A performing SEM-EDS was not the same as lab A performing LIBS, etc.

Table 2: SEM-EDS parameters for tape analysis for interlaboratory exercises #1 and #2.

SEM-EDS Instrumental Parameters				
Lab ID	Lab A	Lab B	Lab C	Lab D
Instrument	Tescan Vega 3	FEI Explorer	Zeiss EVO 40	JEOL JSM 6490LV
Detector	Apollo V EDS	OmegaMax EDS	Oxford INCA EDS	INCA x-Sight
Magnification	50	Variable	180	50
Acceleration Voltage (kV)	25	25	20	25
Working Distance (mm)	15	15	25	15
Take-off Angle (°)	30	37	35	30
Dead Time (%)	30	16	-	30
Counting Time (s)	200	100	152	120

Table 3: LIBS parameters for tape analysis for interlaboratory exercise #1 and #2.

LIBS Instrumental Parameters					
Lab ID	Lab A	Lab B	Lab C	Lab D*	Lab E*
Instrument	J200	J200	RT100	J200	J200
Laser	Nd:YAG	Nd:YAG	Nd:YAG	Nd:YAG	Nd:YAG
	266 nm	266 nm	266 nm	266 nm	266 nm
Laser Energy	100% (19 mJ)	100% (19 mJ)	100% (~30 mJ)	100%	50%
Spot Size (μm)	100	100	100	100	100
Gas Used	Air	Ar	Air	Air	Ar
Shots	403	403	403	403	325
Gate Delay (μsec)	0.9	0.9	0.9	0.5	1.0
Frequency (Hz)	10	10	10	10	10
Stage Speed ($\mu\text{m/s}$)	100	150	100	100	300
Line Length (mm)	4	6	4	4	2

*Data reported for interlaboratory exercise #2

Table 4: LA-ICP-MS parameters for tape analysis for interlaboratory exercise #1 and #2.

LA-ICP-MS Instrumental Parameters			
	LAB A	LAB B	LAB C*
MS Instrument	Agilent 7700x	PE ELAN 6100	PE NEXION 350X
Laser	193 NWR ESI (193 nm)	New Wave ns–Nd:YAG (213 nm)	Applied Spectra ns–Nd:YAG (266 nm)
Laser Energy	0.7 mJ	2.6 mJ	19 mJ
Stage Speed	40 $\mu\text{m/s}$	40 $\mu\text{m/s}$	40 $\mu\text{m/s}$
Spot Size	150 μm	190 μm	200 μm
Repetition Rate	20 Hz	10 Hz	10 Hz
Ablation Mode	Line	Line	Line
Line Length	5.6 mm	4 mm	4 mm
Sampling Time	140 s (2 min 20 sec)	180 s (3 min)	150 s (2 min 30 sec)
Blank Time (Laser Off)	30 sec	40 sec	40 sec
Carrier Gas	Helium	Helium	Helium
Gas Flow	0.8 L/min	0.9 L/min	0.6 L/min

*Data reported for interlaboratory exercise #2

Data Reduction and Statistical Analysis

Data reduction and statistical analyses were performed using Excel 2011 (version 14.7.7, Microsoft Corporation), the Aurora software for LIBS data integration and peak identification (version 2.1, Applied Spectra, Fremont, CA), and Plot2 for Mac (version 2.3.7, Berlin, Germany) for spectral overlay comparisons.

Each data file originally obtained from the instrument was converted into a .csv file for further data processing. The .csv files consisted of a column for the intensity/counts representing the y axis and a column for the measurement variables representing the x axis (e.g. energy in eV for SEM-EDS, mass/charge ratio for LA-ICP-MS in mass scan mode, time in seconds per each isotope for LA-ICP-MS in transient mode, wavenumbers in nm^{-1} for IR, and retention time and mass/charge ratio for Py-GC-MS). The .csv files were used to further graph the data for spectral comparison and for integration of the area under the curve for the selected element peaks, emission lines, and isotopes.

Data Pre-Processing

The data collected for SEM-EDS was in the form of energy spectra (counts vs. x-ray energy). Data pre-processing included background subtraction and estimation of SNR as reported by Ernst et al. [19].

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 pre-processing for LA-ICP-MS for spectral overlay included the removal of non-relevant mass-to-charge peaks originating from polyatomic and isobaric interferences [20] and normalization to the sum of the intensity peaks as a mean to compensate for any shot-to-shot variation and inter-day variations [17]. 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 [17]. 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: ^{27}Al , $^{135, 137}\text{Ba}$, ^{13}C , $^{42, 44}\text{Ca}$, ^{111}Cd , ^{35}Cl , ^{57}Fe , ^{39}K , ^{139}La , ^7Li , $^{24, 26}\text{Mg}$, ^{23}Na , $^{206, 208}\text{Pb}$, $^{121, 123}\text{Sb}$, $^{28, 29}\text{Si}$, $^{118, 119}\text{Sn}$, $^{86, 88}\text{Sr}$, $^{47, 48}\text{Ti}$, ^{232}Th , $^{64, 66}\text{Zn}$, $^{90, 91}\text{Zr}$.

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: $\pm 3s$, $\pm 4s$ and $\pm 5s$, 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 (Table 1). 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 (Table 1) 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) (Table 5). 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.

Table 5: False positive rate (FPR) and false negative rate for the elemental techniques for interlaboratory exercise #1 and #2.

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

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 K α)

and Si (1.740 K α) present in Q3. Sample K1 was not distinguished from Q1 and Q2 using SEM-EDS by laboratory D.

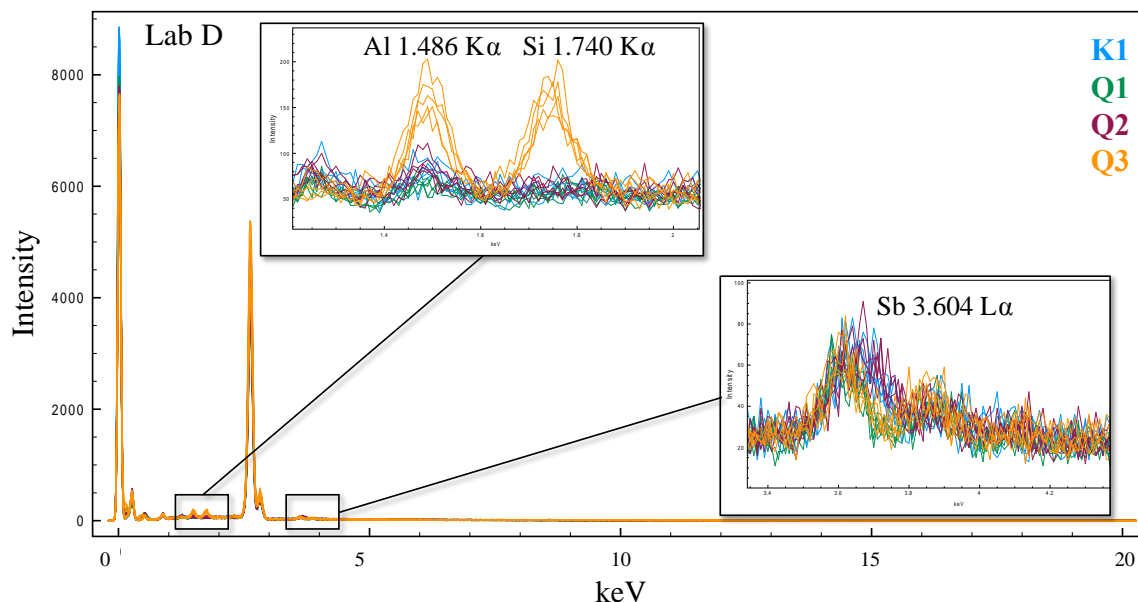


Figure 1: SEM-EDS spectral overlay comparison of K1 vs. Q1, Q2, and Q3 for Lab D for interlaboratory exercise #1. Sample K1 was differentiated from sample Q3 based on the higher amounts of Al (1.486 K α) and Si (1.740 K α) present in Q3. Sample K1 was not distinguished from Q1 and Q2 by SEM-EDS by this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

In contrast, Lab A was able to differentiate the 3M Scotch tapes (Super 88 and 700) (see Table 1). 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 L α) peak, due to the higher amounts of Ca (3.691 K α) in K1 and Q2. This difference in Ca (3.691 K α) 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 L α /Ca K α 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.

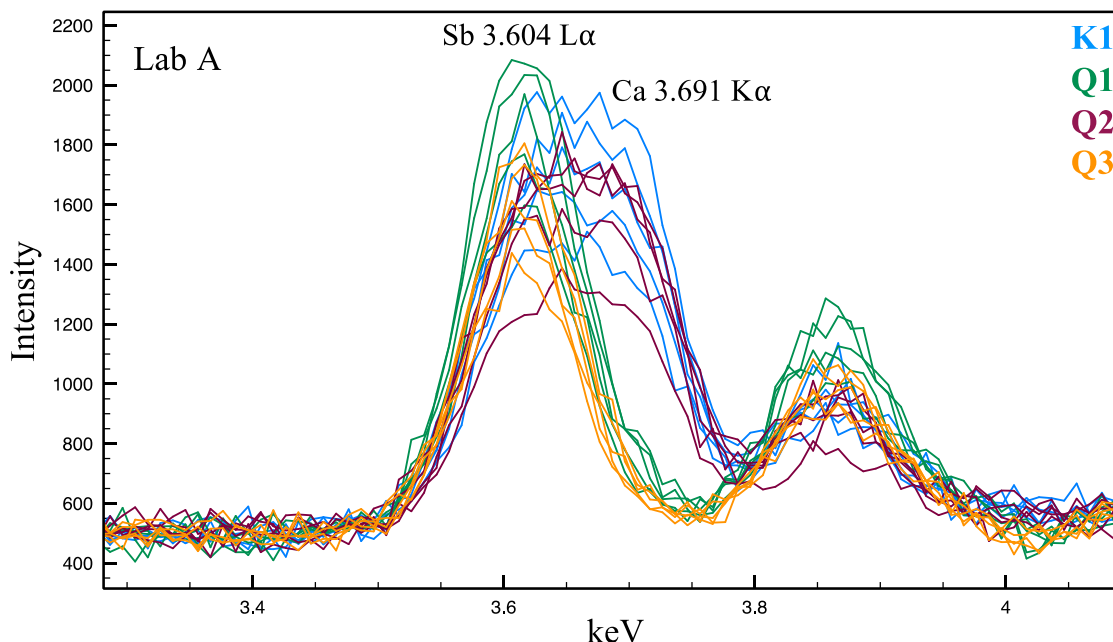


Figure 2: SEM-EDS spectral overlay comparison of K1 vs. Q1, Q2, and Q3 for Lab A for interlaboratory exercise #1. Sample K1 was differentiated from Q2 based on the presence of Ca (3.691 K α) in K1 and Q2.

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 (Table 6). 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 K α 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.

Table 6: Element menu detected for the elemental techniques for each tape pair by the different laboratories in interlaboratory exercise #1.

Lab	Tape Pairs	SEM-EDS	LIBS	LA-ICP-MS
A	K1, Q2	Cl, Ca/Sb, Mg, Al, Si, Zn	Al, Ba, C, Ca, K, Li, Mg, Mo, Na, Sb, Sr, Zn	Al, Ba, Co, Cu, La, Mn, Mo, Ni, Pb, Sb, Sr, Ti, W, Y, Zn
	K2, Q3	Cl, Ca/Sb, Mg, Al, Si	Al, C, Ca, K, Li, Mg, Mo, Na, Sb, Si, Ti	Al, Ba, Co, Cu, La, Mn, Mo, Nd, Ni, Pb, Pr, Sb, Sr, Ti, W, Y, Zn
	K3, Q1	Cl, Ca/Sb, Mg, Al, Si	Al, Ba, C, Ca, K, Li, Mg, Mo, Na, Sb, Sr	Al, Ba, Cu, La, Mn, Mo, Ni, Pb, Sb, Sr, Ti, W, Y, Zn
B	K1, Q2	Cl, Ca/Sb, Mg, Al, Si, Zn	Al, Ba, C, Ca, K, Li, Mg, Mo, Na, Sb, Sr, Ti, Zn	Al, Ba, Ca, Cl, K, Mg, Na, Sb, Si, Sn, Sr, Zn
	K2, Q3	Cl, Ca/Sb, Mg, Al, Si	Al, C, Ca, K, Li, Mg, Mo, Na, Sb, Si, Ti, Zn	Al, Ca, Ce, Cl, Fe, K, Mg, La, Na, Nb, Sb, Si, Ti, Th, Zn
	K3, Q1	Cl, Ca/Sb, Mg, Al, Si, Zn	Al, Ba, C, Ca, K, Li, Mg, Mo, Na, Sb, Sr, Zn	Al, Ba, Ca, Cl, K, Mg, Na, Sb, Si, Sn, Sr, Zn
C	K1, Q2	Cl, Ca/Sb, Mg, Al, Si	Al, Ba, C, Ca, K, Li, Mg, Na, Sr, Zn	
	K2, Q3	Cl, Ca/Sb, Mg, Al, Si	Al, C, Ca, K, Li, Mg, Mo, Na, Sb, Si	-
	K3, Q1	Cl, Ca/Sb, Mg, Al, Si	Al, Ba, C, Ca, K, Li, Mg, Na, Sr	
D	K1, Q2	Cl, Ca/Sb, Mg, Al		
	K2, Q3	Cl, Ca/Sb, Mg, Al, Si	-	-
	K3, Q1	Cl, Ca/Sb, Mg, Al		

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) (Table 1). 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 shown in Table 6. 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 [21-26] 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 5) 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.

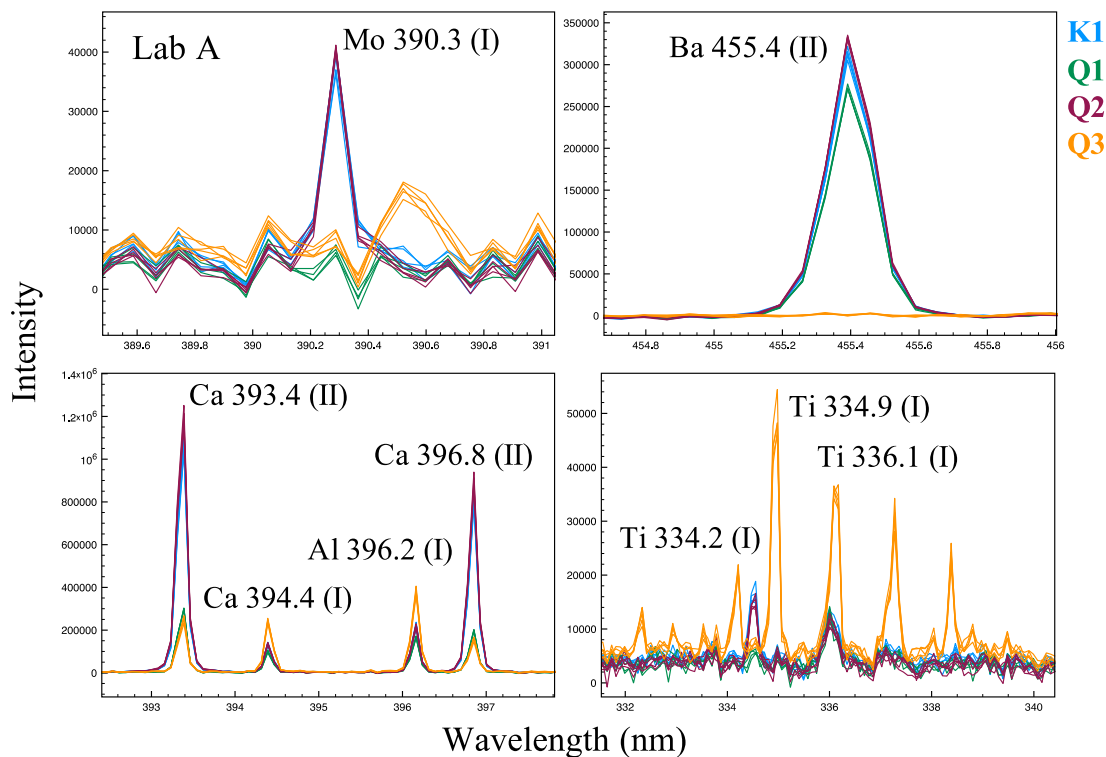


Figure 3: LIBS spectral overlay comparison of K1 vs. Q1, Q2, and Q3 for Lab A for interlaboratory exercise #1. Sample K1 was differentiated from Q1 based on the higher amounts of Mo and Ca in sample K1. K1 was differentiated from Q3 based on Ba, Ca and Ti.

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 (Table 1). 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. Table 6 shows the element menu obtained by LA-ICP-MS for interlaboratory exercise #1 for each pair of tapes. 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 5). 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 [27]. 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.

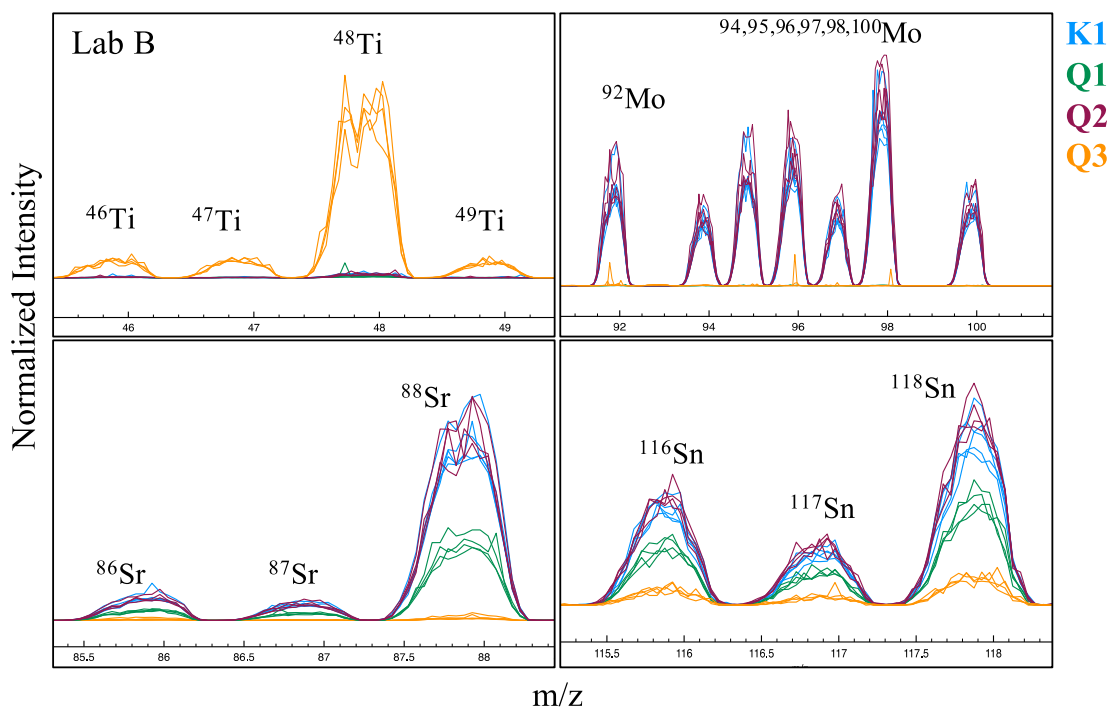


Figure 4: LA-ICP-MS spectral overlay comparison of K1 vs. Q1, Q2, and Q3 for Lab B for interlaboratory exercise #1. K1 was differentiated from Q3 based on Ti, Mo, Sr, and Sn. Sample K1 was differentiated from Q1 based on the higher amounts of Mo, Sr, and Sn in sample K1.

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

Physical examination was performed as part of interlaboratory exercise #1 by all seven participant laboratories. Although each lab used a different method for comparing the tapes, they all grouped the tape pairs belonging to the same rolls. However, physical examination alone was not always able to differentiate the 3M Scotch tapes belonging to different rolls (3M Scotch

Super 88 and 700). Further tests (IR, Py-GC-MS, SEM-EDS) were needed to confirm if there were chemical differences between the tapes. Microscopic and physical examination of tapes typically include the measurement of the thickness and width of the tapes, the number of layers present, and the description of colors of the backing and the adhesive. In addition, the backing texture is described according to its sheen and individual characteristics or imperfections such as dimples, craters, lines, etc. Moreover, the tape ends are evaluated to determine if a fracture match is present.

Infrared analysis was performed by all the laboratories for interlaboratory exercise #1. Out of the seven participant laboratories, six correctly associated the tapes belonging to the same rolls. One laboratory reported false exclusions between K1 and Q2 and between K3 and Q1 based on their IR spectra. Out of the seven laboratories, four could not differentiate the different 3M Scotch tape pairs belonging to different rolls. All laboratories correctly associated the GE tapes (K2 and Q3).

IR spectroscopy is a quick universal technique that provides identification of organic compounds without the need for sample preparation. By using IR spectroscopy, the backing polymer can be identified as polyvinyl chloride, polyethylene, or butyl rubber. Components in the tapes such as phthalates and adipates can also be detected when present at higher concentrations [5, 6, 10, 11]. However, in some instances, FTIR presents some limitations for the analysis of electrical tape backings because primary components of the plasticizer may mask the detection of other components, and the carbon black in the PVC backing creates sloping baselines for the IR spectrum [28].

Pyrolysis gas chromatography was performed by four laboratories. The laboratories compared the chromatograms between tapes. Furthermore, the fragmentation spectra obtained from the mass spectrometry analysis allowed for the identification of specific components in the tapes such as the backing polymer, phthalates, adipates, mixtures of phthalates and adipates, sebacate, trimellitate, among others [5, 6, 9, 11, 12]. Py-GC-MS allowed for the correct association of the tapes belonging to the same rolls, and correctly differentiated the pairs of tapes from different rolls.

The main advantage of Py-GC-MS is that it provides separation (retention time) and identification (mass spectrometry) of the organic compounds present in tapes. However, Py-GC-MS is a destructive and time-consuming technique, and therefore is recommended as the last analytical step in tape examinations.

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 (Table 1). 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, 17].

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. Figure 5 shows the spectral overlay by SEM-EDS for Lab B for interlaboratory exercise #2. Sample K1 was differentiated from sample Q1 based on the higher amounts of Mg (1.254 K α) in K1, and P (2.013 K α), Pb (2.342 M α) and Ca (3.69 K α) present in Q1. Sample K1 was distinguished from Q3 for based on the Ca (3.691 K α) shoulder on the Sb (3.604 L α) peak. K1 was not distinguished from Q2 by SEM-EDS; K1 and Q2 belong to the same tape roll (Table 1).

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 (Table 1) 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 5). 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. The element menu obtained by SEM-EDS analysis for interlaboratory exercise #2 is reported in Table 7.

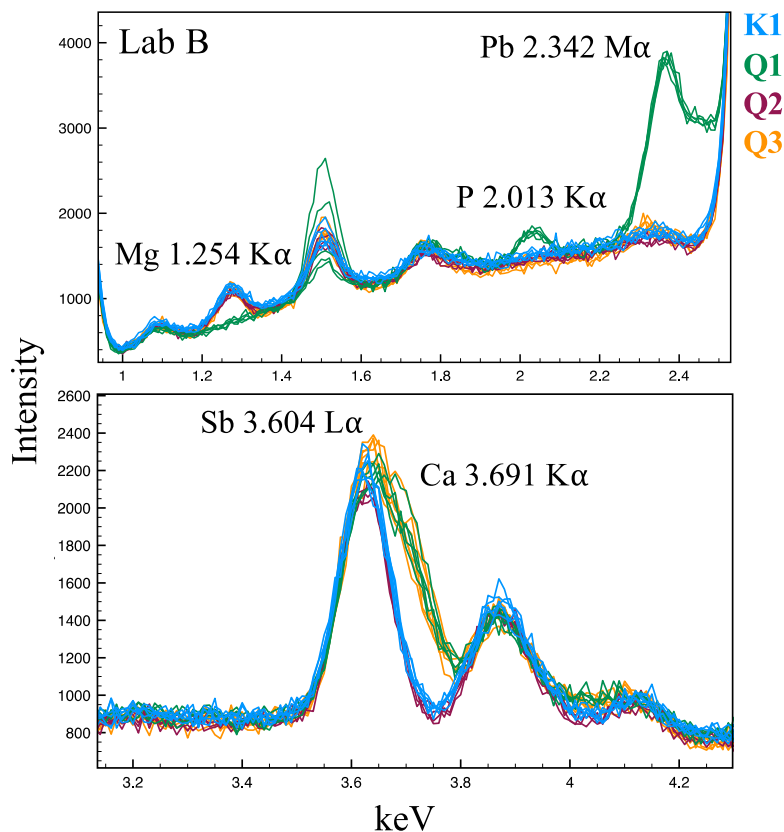


Figure 5: SEM-EDS spectral overlay comparison of K1 vs. Q1, Q2, and Q3 for laboratory B for interlaboratory exercise #2. Sample K1 was differentiated from sample Q1 based on the lower amounts of Mg (1.254 K α) and higher amounts of P (2.013 K α) and Pb (2.342 M α), and the Ca (3.691 K α) shoulder in Q1. Sample K1 was distinguished from Q3 based on the Ca (3.691 K α) shoulder on the Sb (3.604 L α) peak.

Table 7: Element menu detected for the elemental techniques for each tape sample by the different laboratories in interlaboratory exercise #2.

Lab	Tape Pairs	SEM-EDS	LIBS	LA-ICP-MS
A	K1, Q2	Cl, Ca/Sb, Mg, Al, Si	Al, Ba, C, Ca, K, Li, Mg, Mo, Na, Sb, Sr, Zn	Al, Ba, C, Cr, K, Li, La, Mg, Mo, Na, Nb, Ni, Pb, Rb, Sb, Sr, Ti, Tl, W, Y, Zn, Zr
	Q1	Cl, Ca/Sb, Mg, Si, Pb	Al, Ba, C, Ca, K, Li, Mo, Na, Pb, Sb, Zn	Al, Ba, Bi, C, Ca, Cd, Cr, Cu, K, Li, La, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Si, Sr, Ti, Tl, W, Y, Zn, Zr
	Q3	Cl, Ca/Sb, Mg, Al, Si	Al, Ba, C, Ca, K, Li, Mg, Mo, Na, Sb, Sr, Zn	Al, Ba, C, Ca, Cd, Co, Cr, Cu, K, Li, La, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Si, Sr, Ti, Tl, W, Y, Zn, Zr
B	K1, Q2	Cl, Ca/Sb, Mg, Al, Si	Al, Ba, C, Ca, K, Li, Mg, Na, Sb, Si, Sr, Ti, Zn	Al, Ba, Ca, Cd, Cl, Cr, Fe, K, Mg, Na, Pb, Sb, Sn, Sr, Ti, Zn, Zr
	Q1	Cl, Ca/Sb, Mg, Al, Si, Zn, Pb	Al, C, Ca, K, Li, Mg, Mo, Na, Pb, Sb, Si, Ti, Zn	Al, Ba, Ca, Cd, Cl, Fe, K, Mg, Na, Pb, Sb, Sn, Sr, Ti, Zn, Zr
	Q3	Cl, Ca/Sb, Mg, Al, Si, Zn	Al, Ba, C, Ca, K, Li, Mg, Mo, Na, Sb, Si, Sr, Ti, Zn	Al, Ba, Ca, Cd, Cl, Fe, K, Mg, Na, Pb, Sb, Sn, Sr, Ti, Zn, Zr
C	K1, Q2	Cl, Ca/Sb, Mg, Al, Si	Al, Ba, Ca, Cd, Cr, K, Li, Mg, Mo, Na, Sr, Ti	Al, Ba, Ca, Cd, Cl, K, Mg, Na, Pb, Sb, Sn, Sr, Ti, Zn, Zr
	Q1	Cl, Ca/Sb, Mg, Al, Si, Pb	Ca, K, Li, Mo, Na, Pb	Al, Ba, Ca, Cd, Cl, K, Mg, Na, Pb, Sb, Sn, Sr, Ti, Zn, Zr
	Q3	Cl, Ca/Sb, Mg, Al, Si	Al, Ba, Ca, K, Li, Mg, Mo, Na	Al, Ba, Ca, Cd, Cl, K, Mg, Na, Pb, Sb, Sn, Sr, Ti, Zn, Zr
D	K1, Q2	Cl, Ca/Sb, Mg, Al	Al, Ba, C, Ca, K, Li, Mg, Na, Sb	
	Q1	Cl, Ca/Sb, Mg, Al, Si, Pb	Al, C, Ca, K, Li, Mo, Na, Pb, Sb	-
	Q3	Cl, Ca/Sb, Mg, Al	Al, Ba, C, Ca, K, Li, Mg, Mo, Na, Sb	
E	K1, Q2		Al, Ba, Ca, K, Li, Mg, Mo, Na, Sb	
	Q1	-	Al, Ba, Ca, K, Li, Mo, Na, Pb, Sb	-
	Q3		Al, Ba, Ca, K, Li, Mg, Mo, Na, Sb	

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.

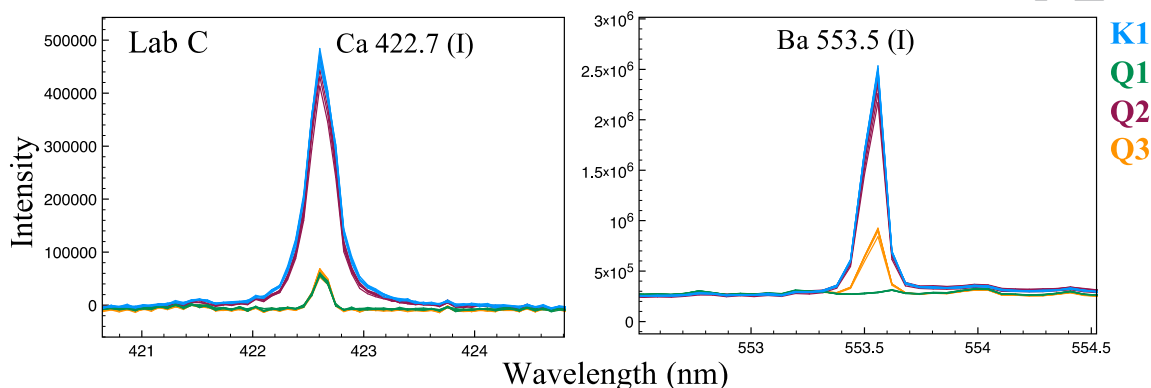


Figure 6: LIBS spectral overlay comparison of K1 vs. Q1, Q2, and Q3 for Lab C for interlaboratory exercise #2. Sample K1 was differentiated from Q1 and Q3 based on the higher amounts of Ca and Ba in K1.

Figure 6 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. Table 8 shows the match criterion results for interlaboratory exercise #2 for LIBS.

Table 8: Distinguished ratios by $\pm 5s$ match criteria comparison for LIBS for interlaboratory exercise #2.

Tape Pairs	Lab A	Lab B	Lab C	Lab D	Lab E
K1, Q1	Mo/Sb, Ca/Sb, Ca/Mo, Al/Ca, Al/Pb, Pb/Sr, Sr/Zn, Na/Mg, Ba/Li	Mo/Sb, Ca/Sb, Ca/Mo, Al/Ca, Al/Pb, Pb/Sr, Sr/Zn, Na/Mg	Ti/Mo, Ca/Mo, Al/Pb, Ba/Li	Mo/Sb, Ca/Sb, Ca/Mo, Al/Ca, Al/Pb, Na/Mg, Ba/Li, K/Li	Mo/Sb, Ca/Sb, Al/Ca, Na/Mg, Ba/Li
K1, Q2	None	None	None	Na/Mg	None
K1, Q3	Mo/Sb, Ca/Sb, Ca/Mo, Al/Ca, Sr/Zn, Na/Mg, Ba/Li	Mo/Sb, Ca/Sb, Ca/Mo, Al/Ca	Ti/Mo, Ca/Mo, Al/Ca, Na/Mg, K/Li	Mo/Sb, Ca/Sb, Ca/Mo, Al/Ca, Na/Mg, Ba/Li, K/Li	Mo/Sb, Ca/Sb, Ba/Li

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 Table 7. 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 (Table 1).

Figure 7 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 Table 7.

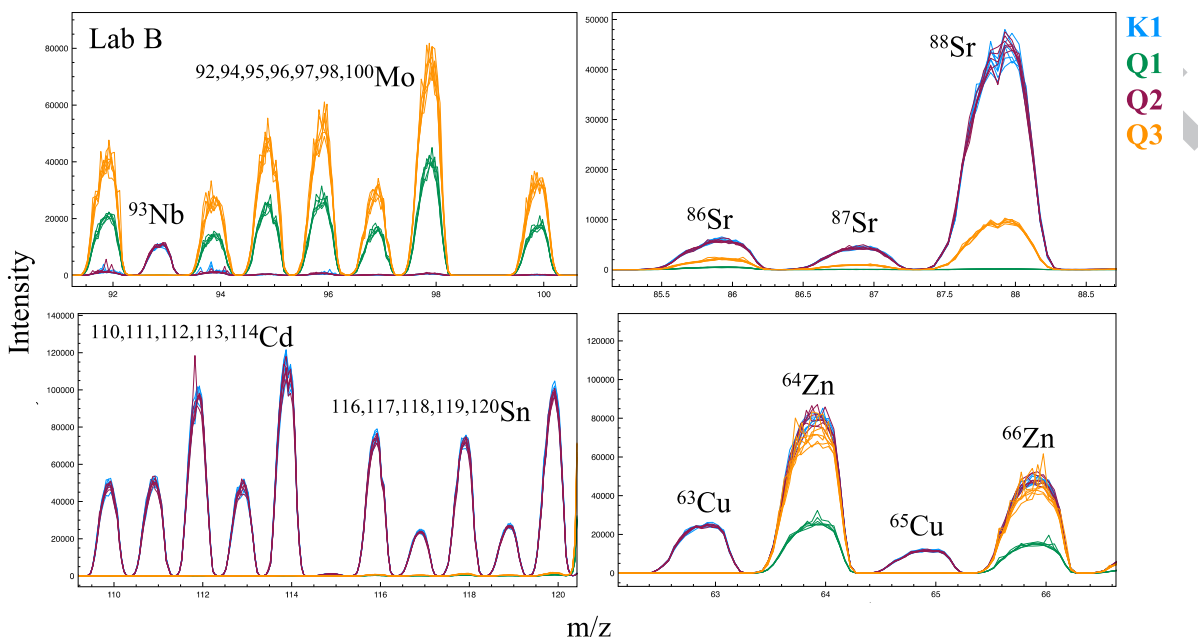


Figure 7: LA-ICP-MS spectral overlay comparison of K1 vs. Q1, Q2, and Q3 for Lab B for interlaboratory exercise #2. Sample K1 was differentiated from Q1 based on their differences in Mo, Sr, Cd, Sn, Cu, and Zn. K1 was distinguished from Q3 based on differences in Mo, Nb, Sr, Cd, Sn, and Cu.

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 compare 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.

Table 9: Distinguished ratios by $\pm 5s$ match criteria comparison for LA-ICP-MS for interlaboratory exercise #2.

Tape Pairs	Lab A	Lab B	Lab C
K1, Q1	Al, Ba, Ca, Fe, K, Mg, Pb, Sr, Ti, Zn, Zr	Al, Ba, Ca, Cd, Cr, Fe, K, Mg, Pb, Sb, Sr, Ti, Zn, Zr	Al, Ba, Ca, Cd, K, Mg, Na, Pb, Sr, Ti, Zn, Zr
K1, Q2	None	None	None
K1, Q3	Ca, Fe, Pb, Ti, Zn	Al, Ba, Ca, Cd, Cr, Fe, K, Mg, Na, Pb, Sb, Sr, Ti, Zn, Zr	Ca, Cd, Na, Pb, Ti, Zn

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. [29-31] This study is a first effort towards standardization of the LA-ICP-MS and LIBS analytical and comparison methods. 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.

Acknowledgments

This project was supported by Award No. 2015-DN-BX-K050 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 manuscript are those of the authors and do not necessarily reflect those of the Department of Justice. Names of commercial manufacturers are provided for identification purposes only, and inclusion does not imply endorsement of the manufacturer, or its products or services by any of the above organizations. This is publication 18-26 of the Federal Bureau of Investigation (FBI), Laboratory Division. Names of commercial manufacturers are provided for identification purposes only and inclusion does not imply endorsement by the FBI. The views expressed are those of the authors and do not necessarily reflect the official policy or position of the FBI or the U.S. Government. A Bridge to Doctorate Fellowship and a Dissertation Year Fellowship were awarded to CM by Florida International University to complete this work.

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. Mehlretter, 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. Mehlretter, 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. Mehlretter, *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. **33**(5): p. 1163-1170.
10. 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.
14. J.F. Carter, P.L. Grundy, J.C. Hill, N.C. Ronan, E.L. Titterton, and R. Sleeman, *Forensic isotope ratio mass spectrometry of packaging tapes*, *Analyst* **129** (2004) 1206-1210.

15. Henning, S., T. Schönberger, 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. **233**(1-3): p. 387-392.
16. 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.
17. Martinez-Lopez, C., et al., *Elemental analysis and characterization of electrical tape backings by LA-ICP-MS*. *Forensic Chemistry*, 2017: p. 96-107.
18. 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.
19. Ernst, T., et al., *Signal- to- noise ratios in forensic glass analysis by micro X- ray fluorescence spectrometry*. *X- Ray Spectrometry*, 2014. **43**(1): p. 13-21.
20. 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.
21. Oace, R.J., S.R. Burns, and E.E. Eastwold, *U.S. 2559990A. Insulating tape*. 1946, Minnesota Mining & Mfg.
22. Hofmann, C.F., C.H. Vondracek, and D.C. Westervelt, *U.S. 3082133A. High temperature electrical insulating tape*. 1957, Westinghouse Electric Corp.
23. Barton, D.M., *US3162722 Electric Tape Insulation*. 1964, Dow Corning Corporation: United States.
24. Miller, J.A., *Pressure Sensitive Adhesive Composition*. 1970, Morgan Adhesives Company.
25. Blance, R.B. and D.M. Gardner, *US3632412 Electrical Tape*. 1972, Monsanto Company: United States.
26. Garcia-Ramirez, R., D.V. Mahoney, and S.O. Ward, *W.O. 2002018507A1. Solventless plasticizer-resistant vinyl electrical tape*. 2002, 3M Innovative Properties Co.
27. Taylor, H.E., *Inductively Coupled Plasma-Mass Spectrometry: Practices and Techniques*. 2000: Academic Press.
28. 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.
29. *Guideline for Using Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy in Forensic Tape Examinations: Scientific Working Group on Materials Analysis (SWGMA)*. *Journal of the American Society of Trace Evidence Examiners*, 2011. **2**(1): p. 122-132.

30. *Guideline for Using Fourier Transform Infrared Spectroscopy in Forensic Tape Examinations: Scientific Working Group on Materials Analysis (SWGMAAT)*. Journal of the American Society of Trace Evidence Examiners, 2011. **2**(1): p. 112-121.
31. *Standard Guide for Using Pyrolysis Gas Chromatography and Pyrolysis Gas Chromatography/Mass Spectrometry in Forensic Tape Examinations: Scientific Working Group on Materials Analysis (SWGMAAT)*. Journal of the American Society of Trace Evidence Examiners, 2014. **5**(1): p. 42-50.

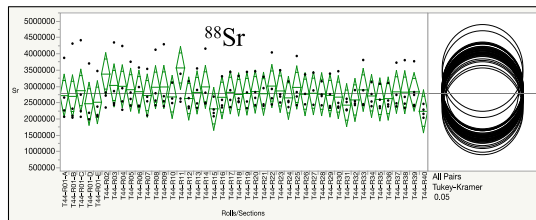
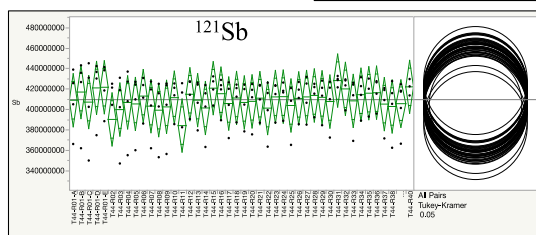
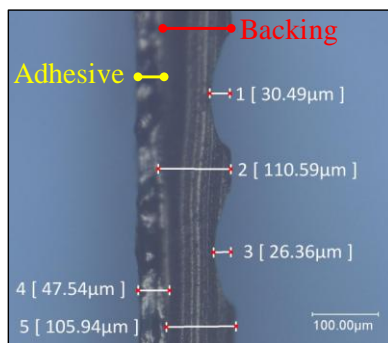
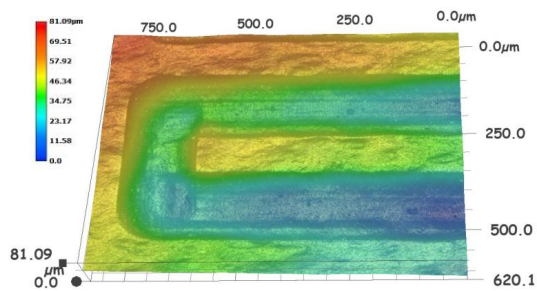
ACCEPTED MANUSCRIPT

Highlights

- Evaluation of physical and microscopic examination, FTIR, Py-GC-MS, and SEM-EDS, LIBS and LA-ICP-MS for the comparison of tape samples in different laboratories.
- Seven (7) laboratories participated in two interlaboratory exercises were designed to study the performance of the different analytical methods for the forensic analysis of electrical tapes.
- 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 to correctly associate the tapes originating from the same rolls.
- A match criterion of $\pm 5s$ allowed to numerically compare LIBS ratios and LA-ICP-MS signal areas for a more objective assessment of the differences between the tape samples.

ACCEPTED MANUSCRIPT

Tape Cross-Section



ACCEPTED MANUSCRIPT