# Methods for the Forensic Analysis of Adhesive Tape Samples by LA-ICP-MS

## Application Note

**Forensic Toxicology**

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## Abstract

**Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) offers great potential as a highly discriminatory technique for the analysis of forensic samples of adhesive tape. Four tape samples and a polyethylene standard were analyzed in this study. By ablating through multiple layers of alternating tape and adhesive glue, an elemental pattern that is unique to that specific tape can be obtained. Being able to present data clearly and unambiguously in a court of law is another consideration for the forensic scientist. Fortunately, LA-ICP-MS data can be presented using various plotting techniques, each designed to discriminate samples with similar visual, physical, and chemical characteristics. These attributes, combined with low levels of detection and high precision, explain the increasing acceptance of LA-ICP-MS for forensic investigation of tapes.**

## Introduction

Adhesive tape samples may be presented as crime scene evidence. In such cases, the forensic scientists may be requested to compare the tape encountered at the crime scene with that found with a suspect or suspects. Traditional techniques for the analysis of tape include visual methods, Fourier transform infrared (FT-IR) for layers analysis, and x-ray fluorescence (XRF) for elemental analysis. Tapes from the same batch, from different manufacturers, of different color and/or morphology, can be discriminated effectively using these methods in many cases. However, for “in-type” discrimination (same brand, different batch and/or same color and matrix), a more rigorous chemical approach is necessary [1].

Standard techniques for the trace elemental analysis of these materials (polyethylene, polypropylene, acetate polymers) typically include time-consuming digestion procedures and hazardous waste by-products. Complete digestion and good trace element recoveries are not always guaranteed.

LA-ICP-MS is an alternative method offering many advantages over standard dissolution techniques. This application note will describe a procedure for the analysis, interpretation, and quantification of these sample types. Though this is a forensic appli-cation, there are clear benefits of this technique for environmental concerns.

### Instrumentation

All the analyses for these experiments were undertaken using an Agilent 7500s ICP-MS. Solid sampling was achieved by introducing a stream of particles generated *in-situ* by direct coupling of a short ultraviolet (UV) laser with the sample surface into the ICP using a stable flow of argon gas. The laser system used was a New Wave Research (Fremont, CA) UP-213AI Nd:YAG operating at the 5th harmonic frequency (213 nm). Operating parameters for each experiment are given in Table 1. For more information on LA-ICP-MS, refer to application note 5989-1565EN [2].

## Operating Parameters

**Table 1. LA-ICP-MS Operating Conditions**

| | | | |
|---|---|---|---|
| **Polyethylene standard** | | | |
| **Laser** | | **ICP-MS** | |
| Line ablation | | RF Power: | 1200 W |
| Spot size: | 100 µm | Plasma gas: | 14 L/min |
| Line length: | 350 µm | Carrier gas: | 0.8 L/min |
| Power: | 1.2 mJ | Acquisition: | Time Resolved Analysis (TRA) |
| Stage speed: | 20 µm/s | Integration: | 50 ms |
| Pulse frequency: | 10 Hz | Masses: | 21 |
| | | Acquire time | 180 s |
| **Adhesive tape** | | | |
| **Laser** | | **ICP-MS** | |
| Spot ablation | | Same as standard | |
| Spot size: | 250 µm | | |
| Power: | 2.2 mJ | | |
| Pulse frequency: | 10 Hz | | |

## Experimental

Calibration of the LA-ICP-MS was carried out using the following standard from Institute for Reference Materials and Measurements, Geel, Belgium.

BCR SRM 680: Trace elements in polyethylene

Adhesive tape samples were acquired from multiple sources. Two samples (P377R, red and P366B, blue) were supplied by VHG Labs, Inc., Manchester, NH. They were part of a group of industrial QC samples sent to the lab for digestion and subsequent aqueous analysis. Tan packing tape brand A and brand B, and 3M and Scotch black electrical tape were purchased at Walgreens, Fremont, CA. Both the tan adhesive tape samples and the black electrical tape samples were visually identical, but produced by two different manufacturers.

Both the polyethylene standard (BCR SRM 680) and the tape samples were attached to a petrographic slide (Figure 1) and placed in the standard UP sample cell for analysis. Tape samples were cut directly from the parent role. For sampling, at least 10 layers of tape were removed as a section from each roll. All tape samples were ablated continuously (250-µm spot) through multiple, alternating layers of the base polymer and sticky adhesive as illustrated in Figure 2. The data was imported into Glitter™ data reduction software for both qualitative and quantitative analysis.

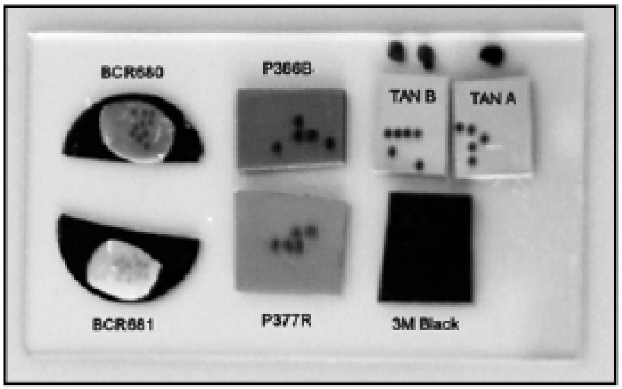

**Figure 1. BCR standards and adhesive tape mounted on petrographic slide showing ablation craters.**

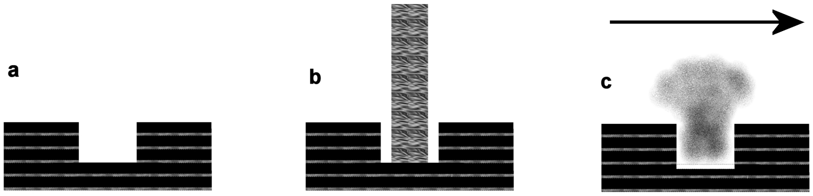

**Figure 2.** **Graphical representation of the ablation process on layered tape samples. a) Layered tape sample after repetitive ablation b) generation of laser plume and c) subsequent removal of laser aerosol within an argon carrier gas stream (arrow).**

## Results

The six tape samples and a polyethylene standard (BCR SRM 680) were analyzed. Five repetitive analyses for each sample and standard were performed. The time-resolved layer analysis (Figure 3) was evaluated to determine the most appropriate way to integrate the data. By ablating through multiple layers of alternating tape and adhesive glue, a unique elemental pattern can be visualized. These elemental "wave-forms" appear to be interlaced or "out of phase" with one another. One set of elements (Al, Mn, Co, and Sb) appears to be associated with the tape backing material, as their signal rises immediately after the start of the ablation cycle. The second set of elements (Cr, Zr, La, Ce, and Pb) appears to be associated with the adhesive glue, as their signals trail the first set by 10 seconds. The lines continue out of phase for the remainder of the ablation cycle. These data were integrated over the entire period of ablation using the $^{13}$C profile as a reference. The trace element concentrations for the P366B and P377R samples were calculated using the BCR SRM 680 (Table 2), and elemental relationships were characterized using a stacked bar graph (Figure 4).

In a previous study (Dobney et al) [1], tape samples were acid digested and the aqueous aerosol analyzed. It was determined that the polymeric base material (PP, PE, and PVC) was difficult to get into solution, was more prone to acid-based matrix interferences, and was chemically less interesting than the adhesive glue. Therefore, trace elements were quantified in the adhesive glue only. By ablating through multiple layers, it is possible to integrate the adhesive elements independently from the elements in the tape backing (data not shown) without any of the difficulties inherent with aqueous digestion.

Ternary plots compare the relationship between three components in a system. Each corner of the plot represents 100% of the labeled component. A data point in the center of the plot signifies that the sample is of equal composition for all three constituents. Ternary plots, more technical in nature compared to bar charts, can discriminate different sample types from one another as well as display sample reproducibility. Tight clustering of sample types describes good sampling precision and data reliability. Figure 5a describes the relationship between $^{27}$Al, $^{121}$Sb, and $^{137}$Ba for the six tape samples characterized here. Although good separation is possible for four of the six tape samples, further discrimination (Figure 5b) is necessary to discriminate the remaining two Tan tape samples by changing the parameters of the ternary plot. In this way, clear separation may be accomplished between samples that are visually identical.

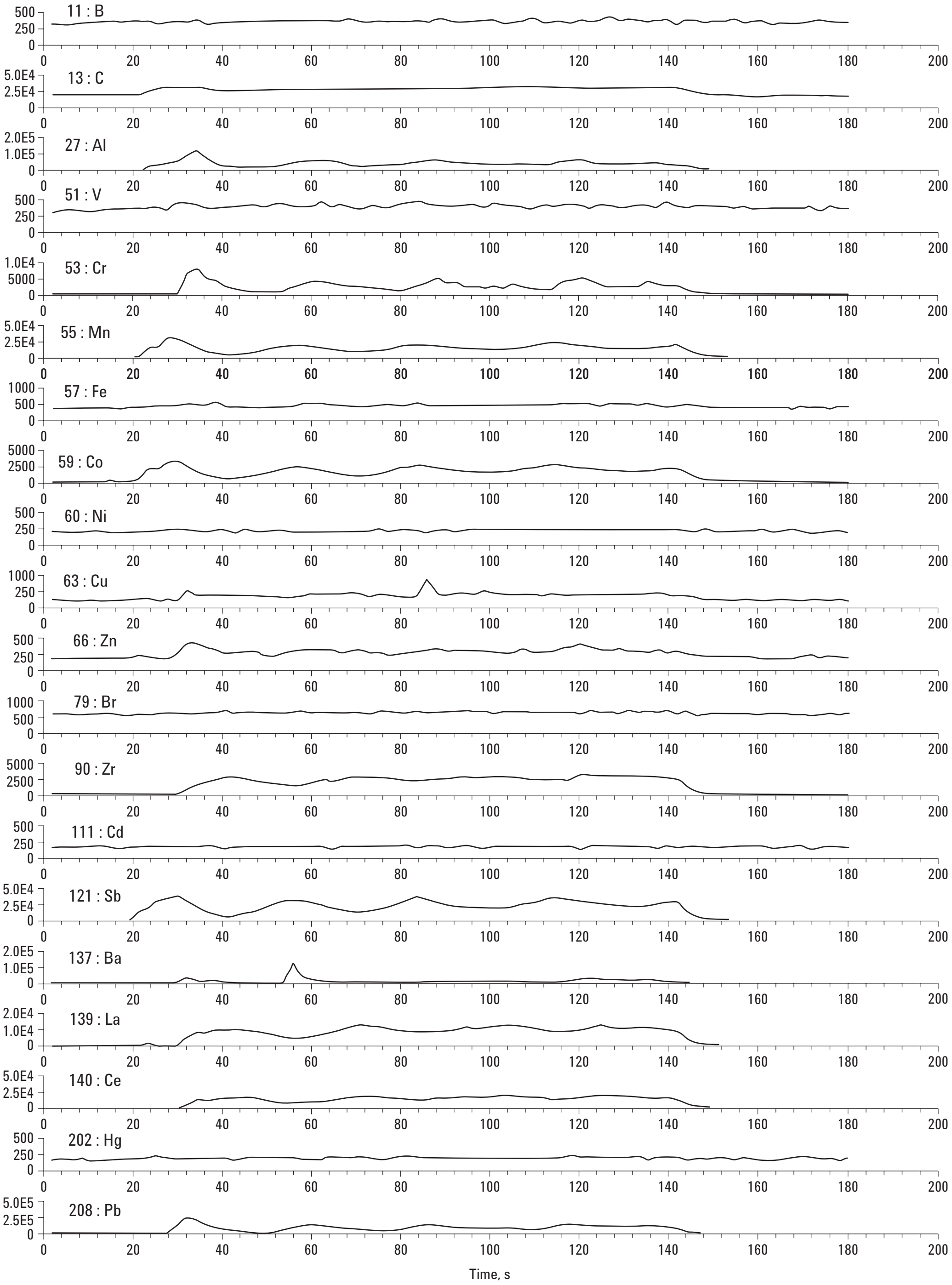

**Figure 3.** **Time resolved layer analysis of colored (blue and red) electrical adhesive tape. Agilent ChemStation time resolved output format of a multi-element profile through successive tape layers. Notice how certain elemental signatures have delayed rise times. Elements within the tape matrix and the adhesive matrix are "out of phase" with respect to each other. Al, Mn, Co, and Sb rise with the onset of the ablation start point (t + 20s). Cr, Zr, La, Ce, and Pb first rise approximately 10 seconds later.**

**Table 2. Quantitative Analysis of Trace Elements in Polyethylene (BCR SRM 680), and the Two Tape Samples (P366B and P377R). Quantitative Data Was Reduced Using Glitter Data Reduction Software.**

**BCR**

| Element | Mean | SD | Agreement % |
|---|---|---|---|
| Al 27 | 51.4 | 0.4 | 100.7 |
| Cr 53 | 114.5 | 0.1 | 99.9 |
| Cu 63 | 118.4 | 1.9 | 99.5 |
| Br 79 | 798.9 | 8.8 | 98.9 |
| Cd 111 | 135.2 | 12.8 | 96.0 |
| Sb 121 | 6.3 | 0.2 | 101.1 |
| Ba 137 | 2639.0 | 132.8 | 97.1 |
| Hg 202 | 24.4 | 0.7 | 96.5 |
| Pb 208 | 107.3 | 3.2 | 99.7 |

**P366B**

| Element | Mean | SD |
|---|---|---|
| Al 27 | 585.2 | 25.2 |
| Cr 53 | 2.5 | 0.7 |
| Cu 63 | 1016.7 | 32.5 |
| Br 79 | 17.2 | 3.3 |
| Cd 111 | 18.3 | 1.1 |
| Sb 121 | 1162.2 | 22.1 |
| Ba 137 | 9.8 | 2.7 |
| Hg 202 | 1.8 | 0.3 |
| Pb 208 | 2.2 | 0.7 |

**P377R**

| Element | Mean | SD |
|---|---|---|
| Al 27 | 611.7 | 77.8 |
| Cr 53 | 215.1 | 29.2 |
| Cu 63 | 4.2 | 0.7 |
| Br 79 | 30.9 | 15.4 |
| Cd 111 | 22.9 | 4.3 |
| Sb 121 | 1139.8 | 90.8 |
| Ba 137 | 877.3 | 87.4 |
| Hg 202 | 3.2 | 1.0 |
| Pb 208 | 3067.8 | 397.2 |

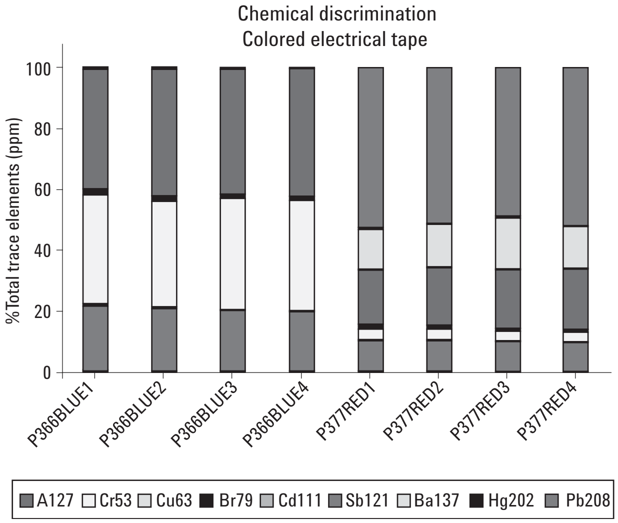

**Figure 4.** **Stacked bar plot of two polypropylene tapes (blue and red) from the same manufacturer. The data in the chart is derived from Table 2.**

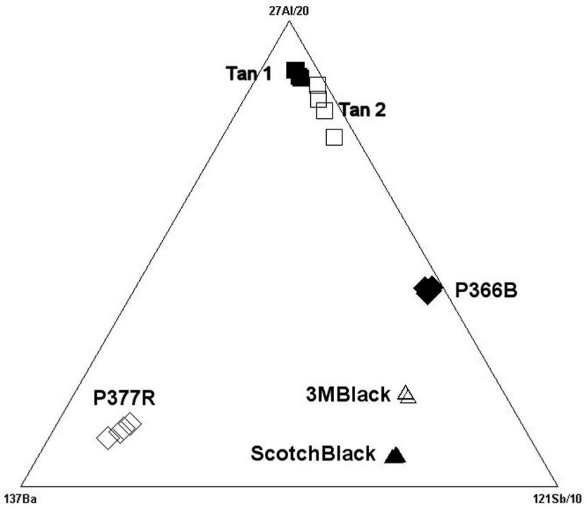

**Figure 5a.** **Ternary Plot of Adhesive tape data (integrated counts per second). Ternary plots are an effective way to discriminate subtle differences in sample populations, especially when multiple data point display is desirable.**

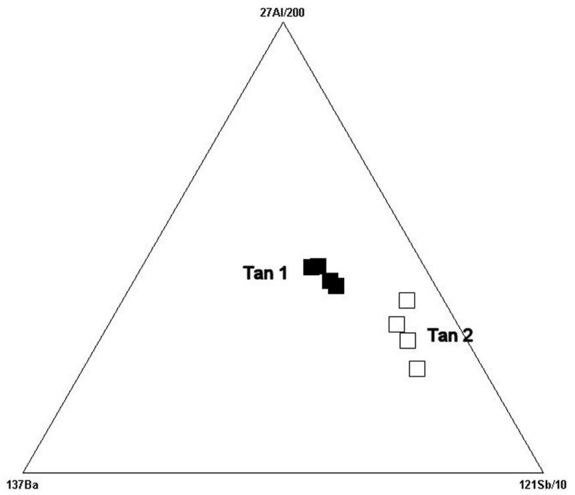

**Figure 5b.** **By changing the parameters of ternary plots, it is possible to further discriminate subtle differences in chemistry between visually identical samples.**

## Conclusion

LA-ICP-MS is an *in-situ* analytical method capable of sampling through layered materials. Through the direct analysis of adhesive tape, three-dimensional chemical characterization is possible. Preliminary evidence suggests that there is an advantage to analyzing both the substrate and the adhesive in these samples.

Through the implementation of various plotting techniques, it is possible to discriminate samples with similar visual, physical, and chemical characteristics. By combining powerful, *in-situ* micro analysis, low levels of detection, high precision, and clear and easily understandable diagrams, LA-ICP-MS is becoming an increasingly important weapon in the arsenal of forensic science.

## References

1. A. Dobney, W. Wiarda, P. de Joode and Gerard van der Peijl, Forensic Tape Investigations, Presentation at 2nd EAFS Meeting, 2000 Sept 24, Cracow.
2. Lawrence M. Neufeld, “Introduction to Laser Ablation ICP-MS for the Analysis of Forensic Samples”, Agilent Technologies publication 5989-1565EN www.agilent.com/chem.

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