

Analysis of duct tapes by thermal desorption and pyrolysis mass spectrometry and X-ray-fluorescence spectroscopy

Introduction

The identification of pressure-sensitive tapes such as duct tape and electrical tape is an important forensic application. Here we show the application of thermal desorption and pyrolysis combined with Direct Analysis in Real Time (DART) mass spectrometry to distinguish between manufacturers and brands of duct tapes. X-ray fluorescence (XRF) provides complementary information about the atomic composition of the different tapes.

Experimental

Samples

Seven duct tape samples were analyzed by mass spectrometry and six by XRF: two Ace® Hardware tapes (one black and one gray), two 3M Scotch® duct tapes (one gray and one white), Rite-Aid® gray duct tape, Gorilla® black duct tape and Loctite Sumo black duct tape (not available when the other tapes were analyzed by XRF).



Figure 1. Duct tapes analyzed in this study



Thermal desorption/ pyrolysis DART mass spectrometry

Mass spectra were acquired by using a JEOL AccuTOF-DART® 4G mass spectrometer (Figure 2) equipped with a Biochromato, Inc. ionRocket thermal desorption and pyrolysis system (<http://biochromato.com/ionrocket/>).



Figure 2. The ionRocket thermal desorption/pyrolysis system mounted on the AccuTOF-DART 4G mass spectrometer

A small sample of each duct tape (roughly 1 mm in diameter) was placed into a disposable copper sample stage (or “pot”) for the *ionRocket* (Figure 3).

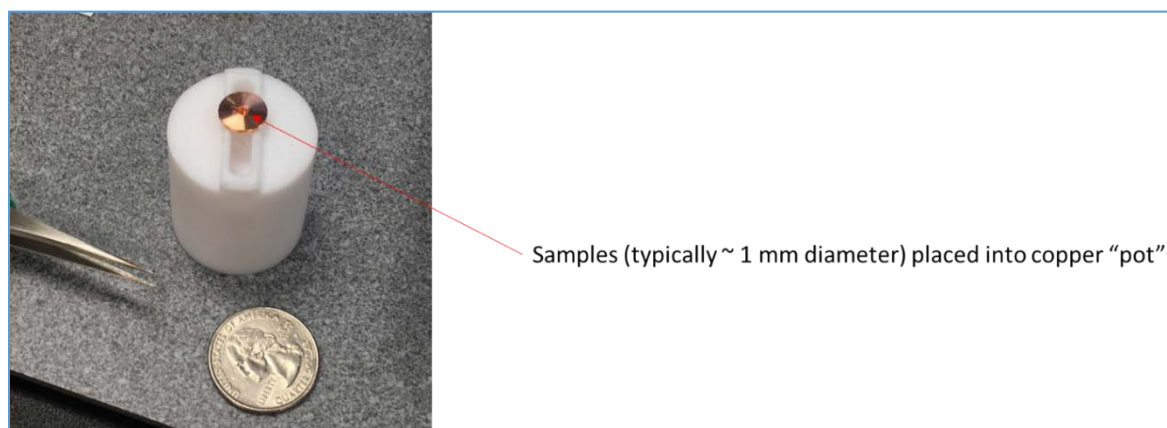


Figure 3. A copper pot used as a sample holder for the *ionRocket*

The copper sample stage was placed onto the *ionRocket* heater (Figure 4) and moved into position between the exit of the DART ion source and the sampling orifice of the *AccuTOF-DART 4G* mass spectrometer. A glass tee positioned above the sample (Figure 5) guides the thermal desorption and pyrolysis products into the DART gas stream.

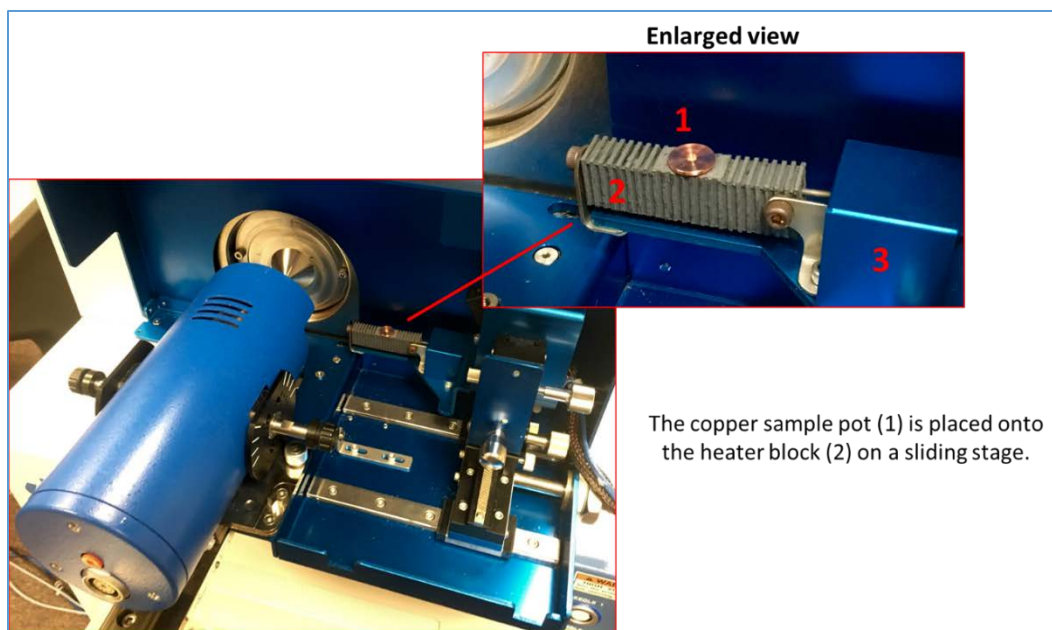


Figure 4. A sample mounted onto the ionRocket heater block.

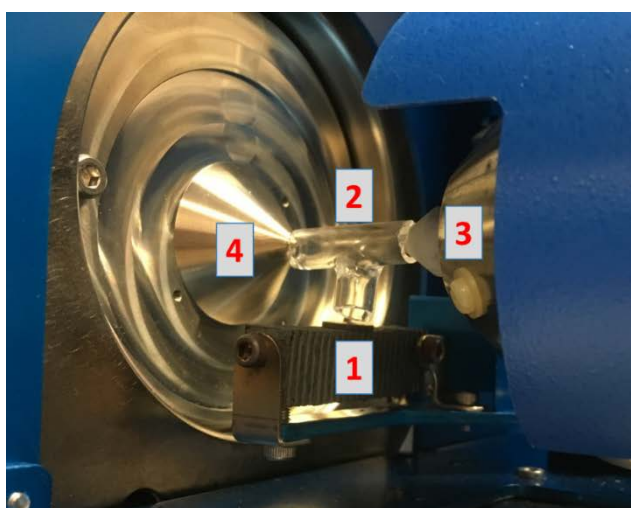


Figure 5. A sample mounted on the heater block, positioned below a glass tee.

The temperature ramp was programmed from ambient temperature to 600°C at a rate of 100°C min⁻¹. Mass spectra were acquired at a resolving power of 10,000 in positive-ion mode at a spectral acquisition rate of 1 spectrum per second for the m/z range 50-1000.



X-ray fluorescence (XRF)

A JEOL *Element Eye* (JSX-100S) benchtop x-ray fluorescence spectrometer (Figure 6) was used for all measurements using the *Quick and Easy Organic Analysis - Vacuum* solution. The vacuum condition was used to enhance sensitivity of light elements like silicon and aluminum. Measurement time was 60 seconds and a collimator setting of 9mm was set.



Figure 6. “Element Eye” benchtop x-ray fluorescence spectrometer

Results

Thermal desorption/DART/MS

Thermal desorption/DART mass spectra showed a clear and reproducible temperature dependence of polymer additives, natural rubber adhesive and pyrolysis products for each tape (Figure 7).

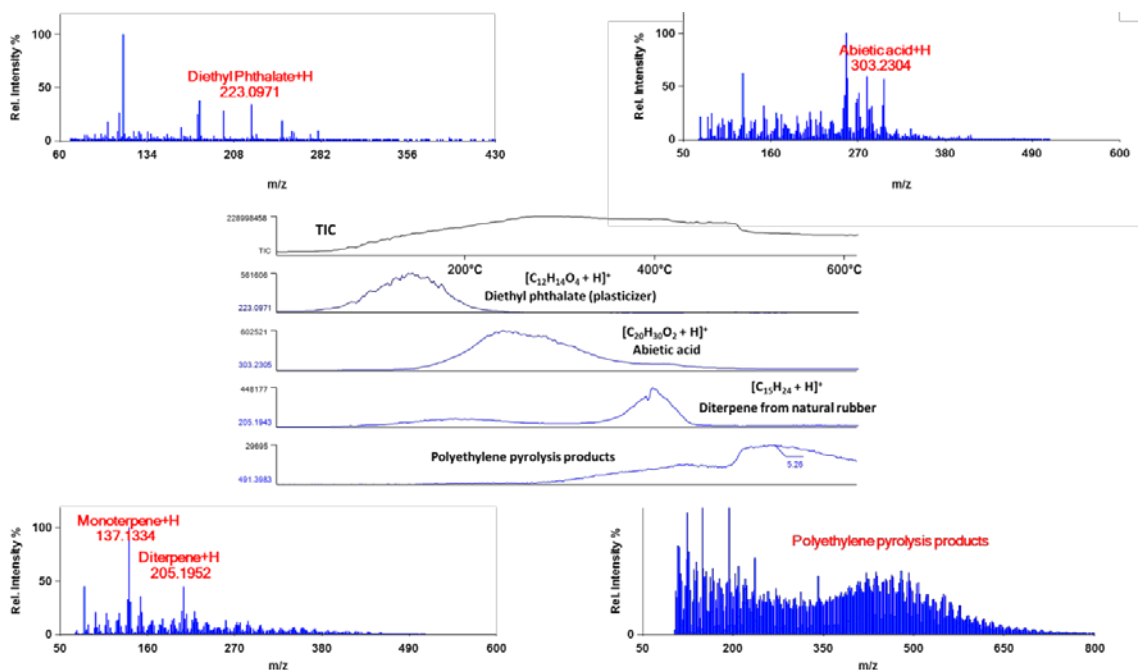
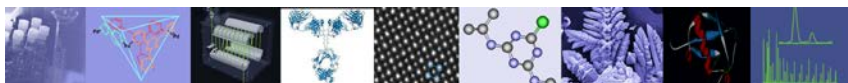


Figure 7. Temperature dependence and mass spectra for selected components



The thermal desorption profiles for certain components (for example abietic acid) differed reproducibly between samples (Figure 8).

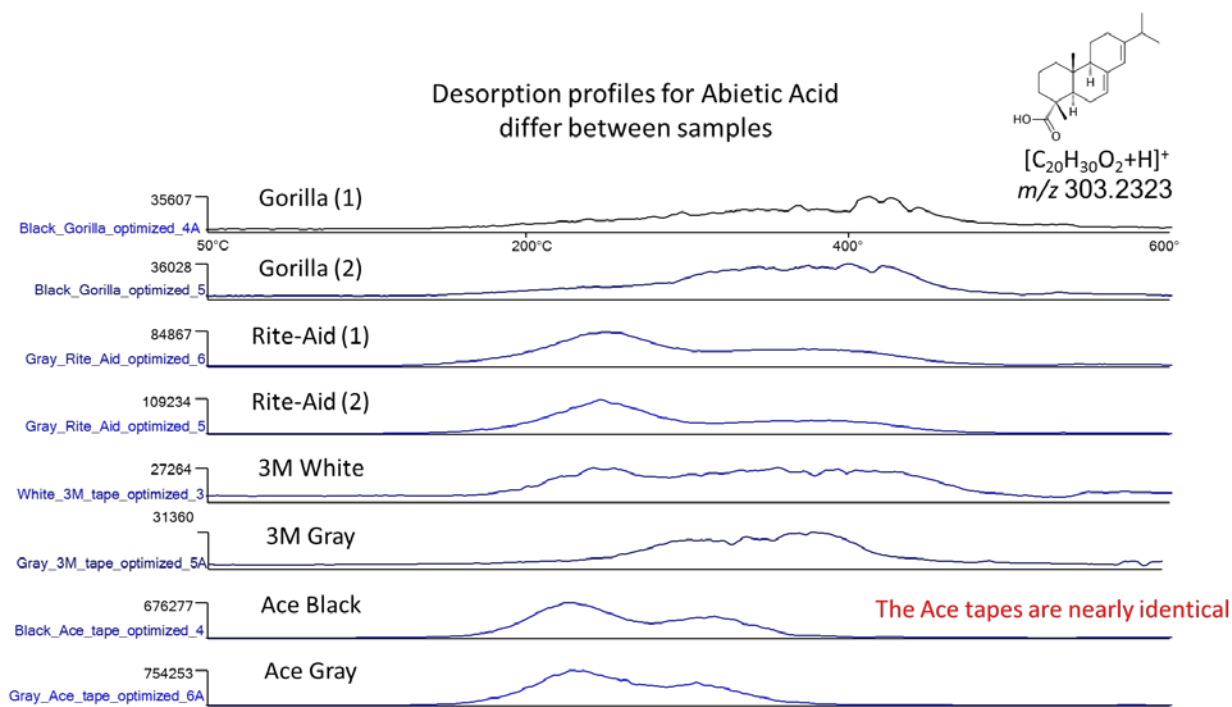


Figure 8. Thermal desorption profiles for abietic acid in different tapes.

The two Ace[®] duct tapes showed nearly identical mass spectra and thermal desorption profiles, with one exception: a peak at m/z 247.168 with the elemental composition $[C_{16}H_{22}O_2 + H]^+$ was only present at significant levels in the gray tape, but not in the black tape.



Chemometric analysis of the thermal desorption mass spectra summed over the temperature range 144-166°C showed good separation between the different duct tapes. This temperature range was chosen because it highlighted differences between the additives in the different tapes without including excessive data from the natural rubber adhesive or pyrolysis products. The heat map (Figure 9) shows differences between the duct tapes. Kernel discriminant analysis (KDA, Figure 10) gave 100% accuracy for leave-one-out cross validation (LOOCV) using four principal components.

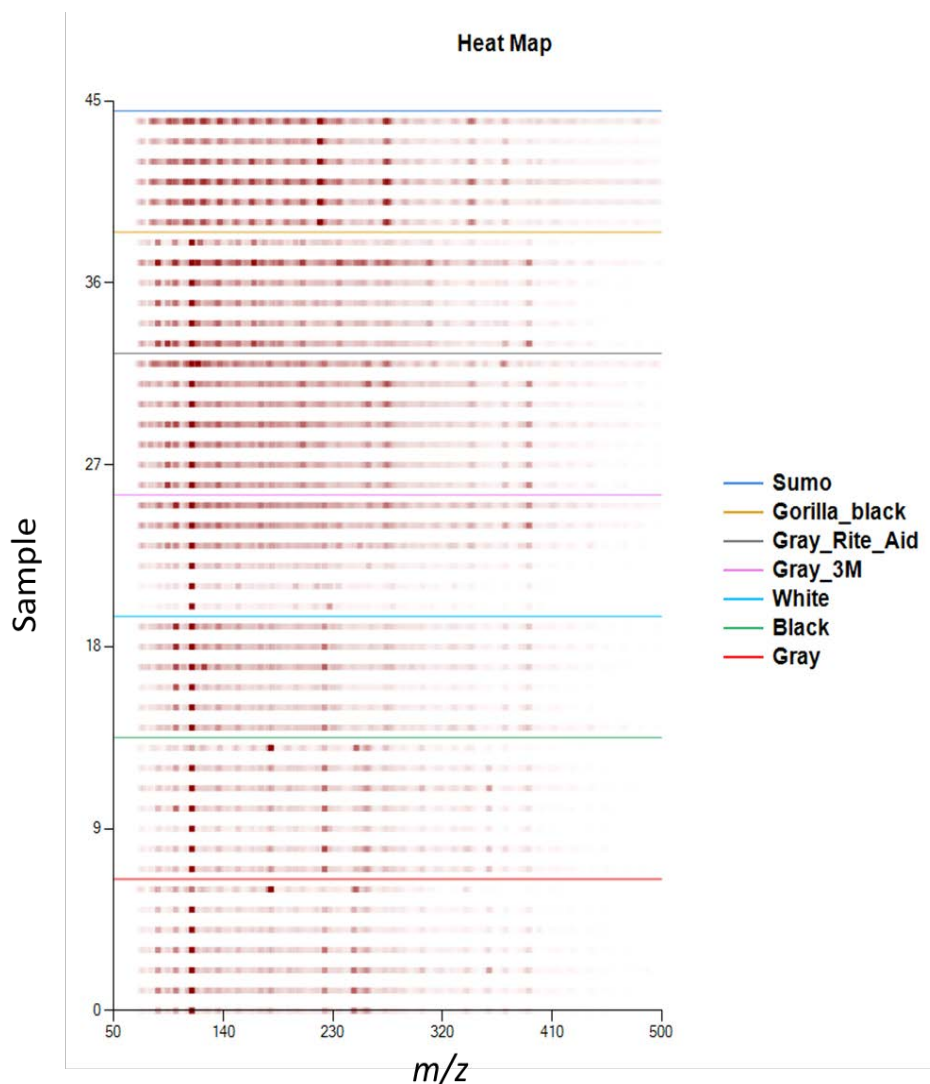


Figure 9. Heat map showing abundances for peaks in the mass spectra for each duct tape class.

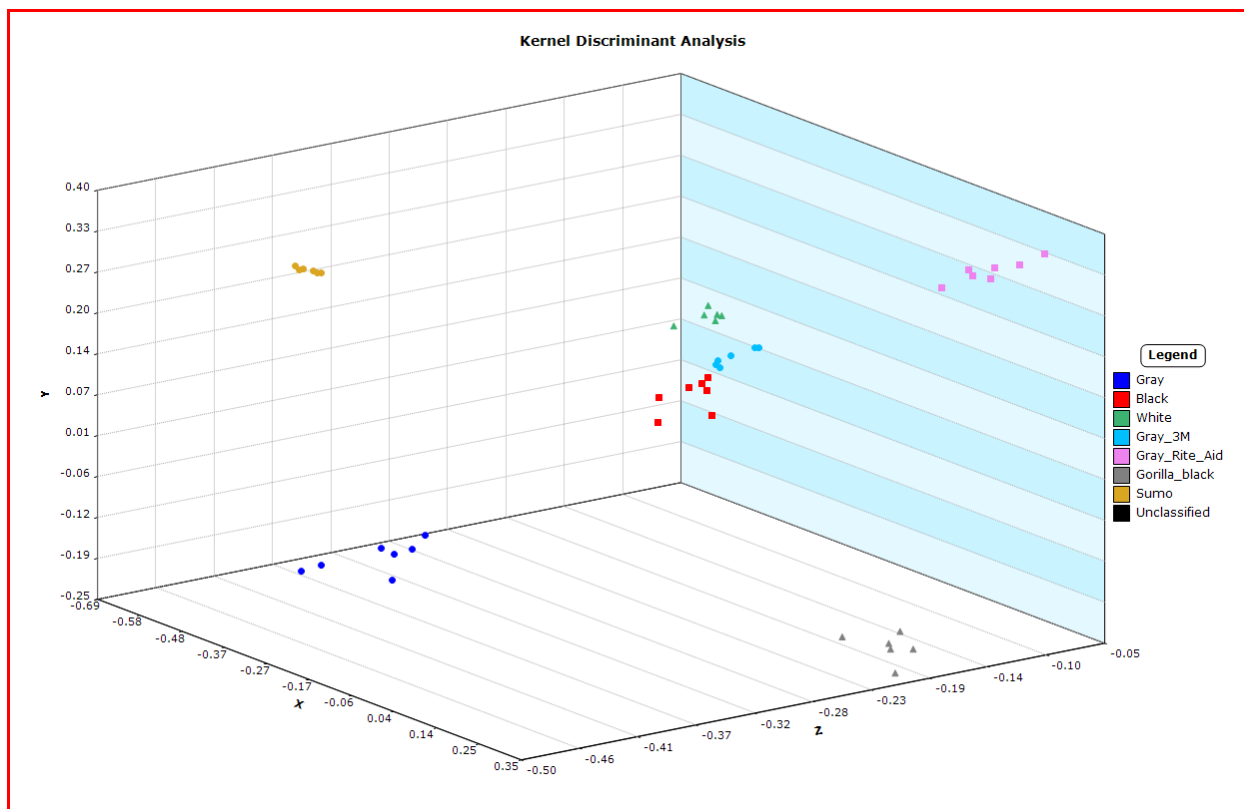


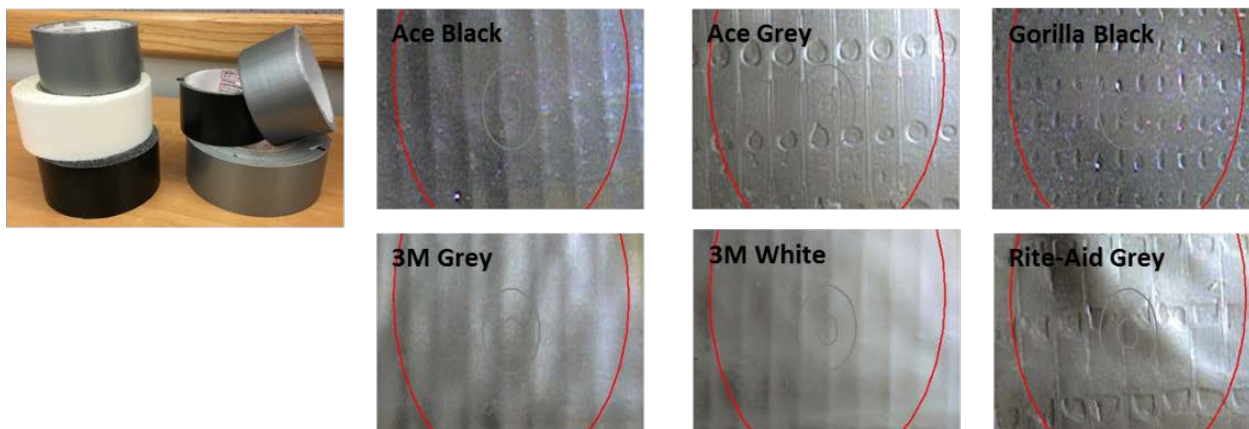
Figure 10. Kernel discriminant analysis of thermal desorption/pyrolysis DART mass spectra for seven duct tapes over the temperature range 144-166°C



XRF

The XRF spectra showed differences in the atomic compositions for each tape. The gray tapes all contained significant amounts of aluminum, while the white tape showed abundant titanium (probably from TiO_2 pigment). The black tape showed abundant Ti and also abundant Ca. A summary of the atomic compositions for each of six tapes is shown in Figure 11 along with images of the region analyzed.

Tape – EDXRF Summary



	Weight %					
Element	3M White	3M Grey	Gorilla Black	Rite-Aid Grey	Ace Black	Ace Grey
Al	0.08	0.50	0.02	0.92	0.06	0.50
Si	0.20	0.32	0.01	0.01	0.29	0.01
P	0.01	0.01			0.01	
S	0.00		0.05		0.02	
Ca	6.46	6.63	8.21	0.71	3.47	1.67
Ti	2.32	0.25	0.08	0.59	0.51	0.26
Fe	0.02	0.02	0.02	0.00	0.02	0.01

Figure 11. Summary of XRF analysis of six duct tapes

Conclusion

Mass spectra and thermal desorption profiles measured with the Biochromato *ionRocket* thermal desorption/pyrolysis system mounted on the JEOL *AccuTOF-DART* mass spectrometer showed clear and reproducible differences between the six different duct tapes. XRF data from the *Element Eye* showed distinct differences between each tape and provided information about the inorganic pigments used to color the tapes.