AccuTOF ™ with ***DART ™***

Direct Analysis of Adhesives

DART can be used with a heated gas stream to rapidly pyrolyze and identify low-volatility materials such as adhesives and resins, directly on surfaces. Although these materials are not pure compounds, a library of DART mass spectra can be created and searched to identify materials, and exact mass measurements coupled with accurate isotopic abundances can be used to identify unknown components. Examples are shown here for cured and uncured epoxies and acrylate adhesives on metal and glass.

All samples were analyzed by acquiring positive-ion mass spectra with the DART source operated with helium and a gas heater setting of 450° C (helium temperature ~350° C). All mass spectra were measured over the *m/z* range 60-1000 at a resolving power of 6000. Following each analysis, a glass rod coated with PEG 600 was placed in front of the DART source to provide a calibration for exact mass measurements. A nominal-mass library of adhesive mass spectra was created by using the software link to the NIST version 2.0 mass spectra database search program. All figures shown here are copied from that library and only integer masses are shown although exact masses were recorded for all peaks.

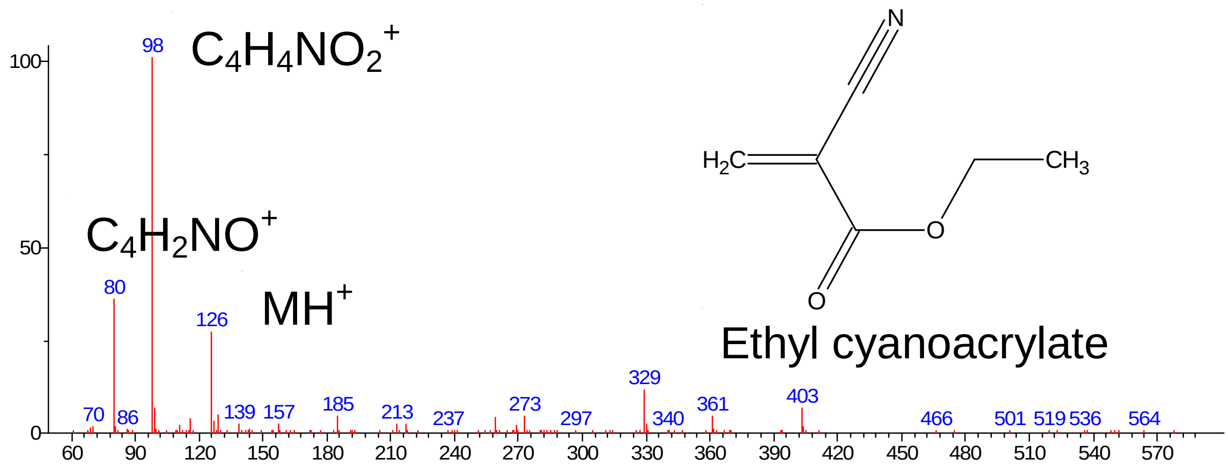

Figure 1. Cyanoacrylate adhesive on metal (Product 1)

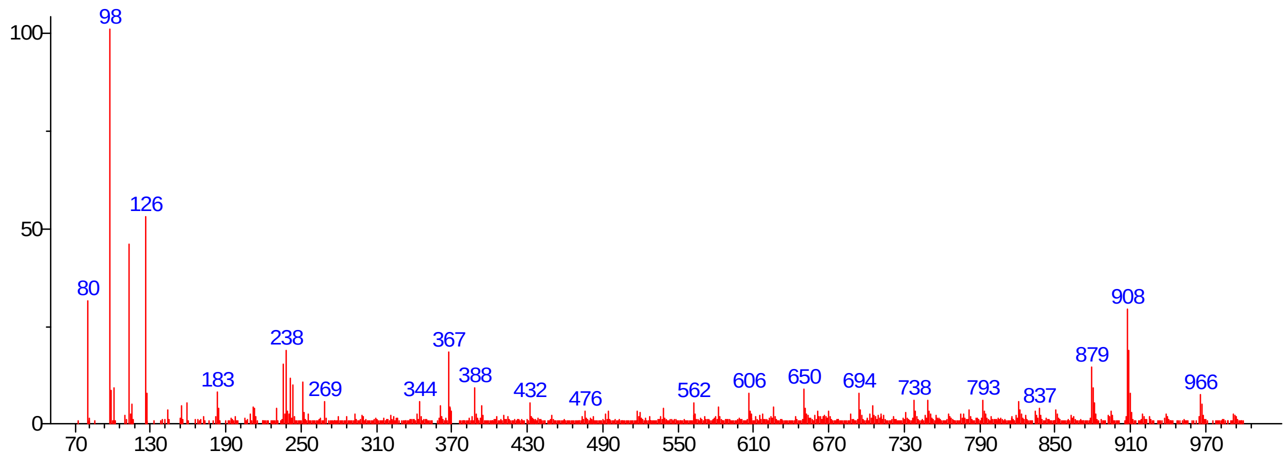

Figure 2. Cyanoacrylate adhesive on metal (Product 2)

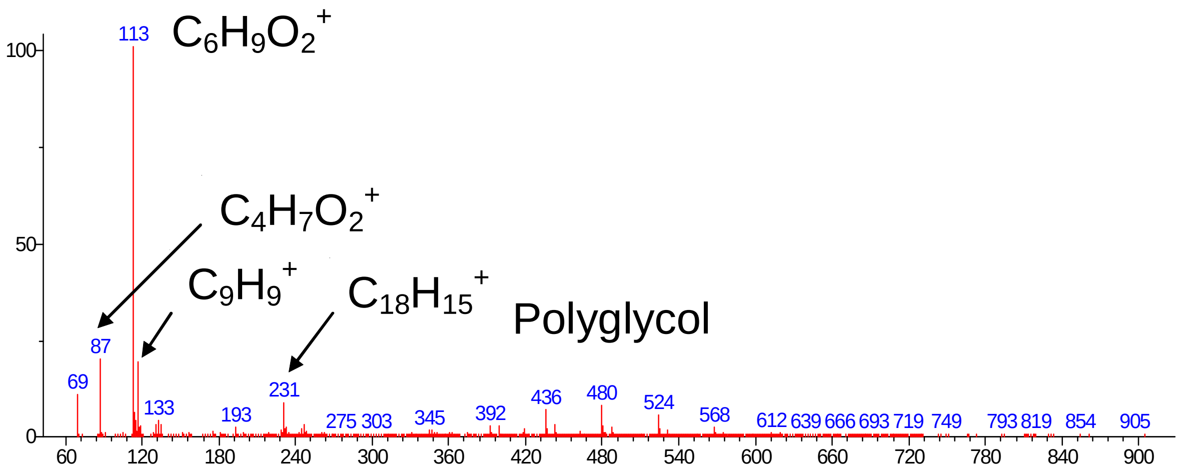

Figure 3. Methacrylate ester adhesive on glass (Product 3)

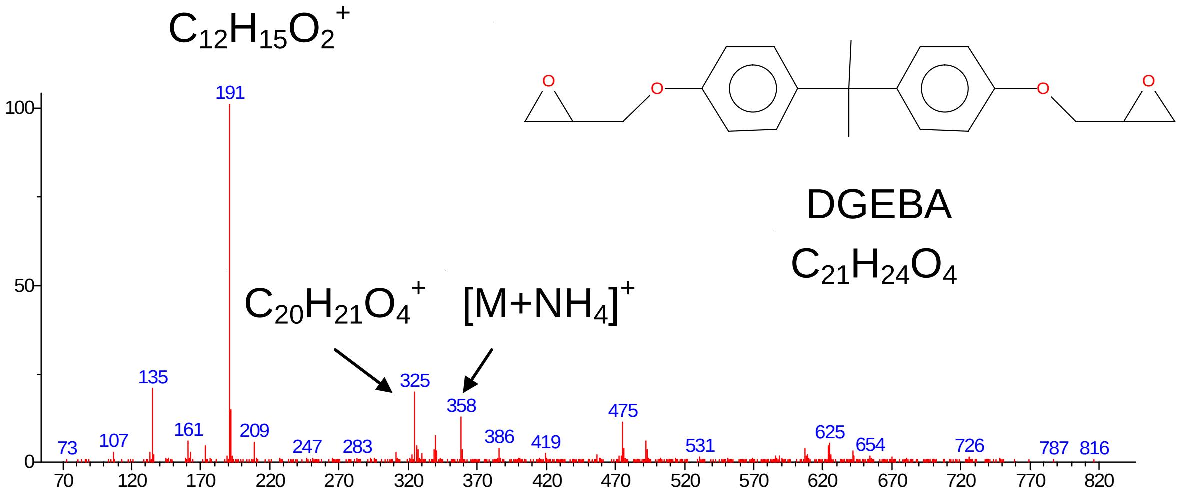

Figure 4. Epoxy resin (black component, uncured)

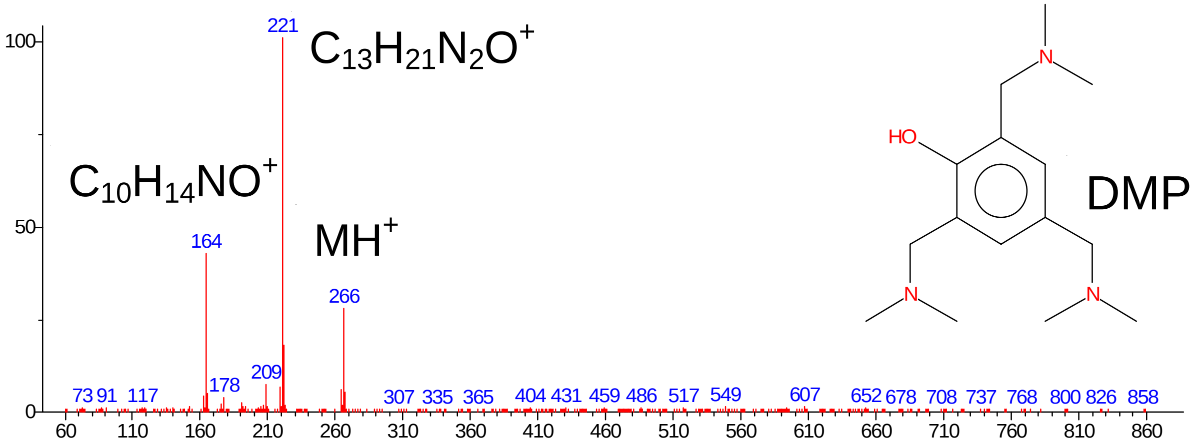

Figure 5. Epoxy hardener (white component)

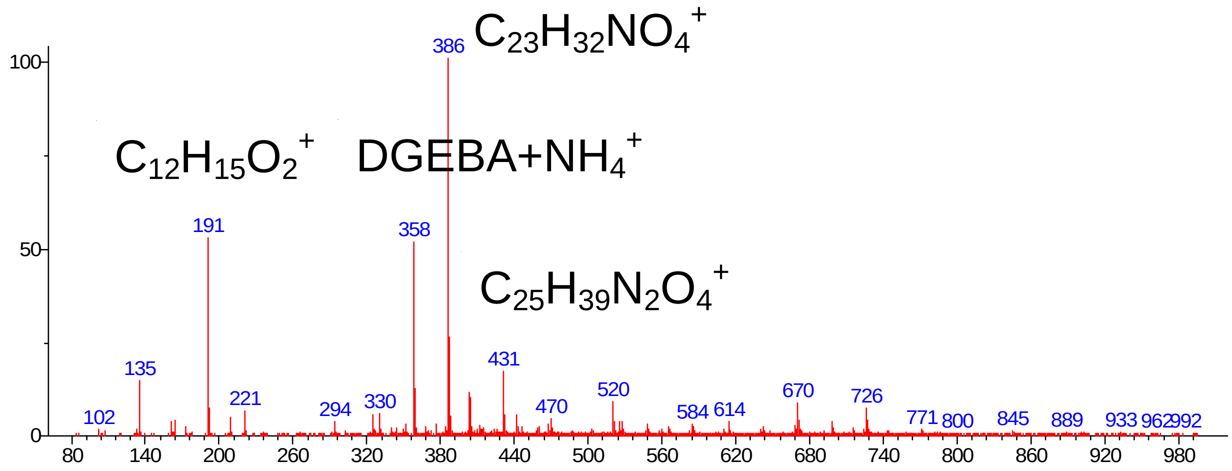

Figure 6. Cured epoxy

Both cyanoacrylate products show ethyl cyanoacrylate (*m/z* 126.0555) and fragment ions $C_4H_2NO^+$ (*m/z* 80.0136) and $C_4H_4NO_2^+$ (*m/z* 98.0242). Product 2 shows an additional peak at measured *m/z* 113.0602. This differs by only -0.05 u from the calculated *m/z* for $C_6H_9O_2$, tentatively assigned as $[M+H]^+$ for allyl methacrylate. Product 2 also shows a series of high-mass peaks that differ by 44.0262, indicative of ethylene oxide based polymer subunits. A product described as a "methacrylate ester" (Figure 3) was dominated by the same $C_6H_9O_2^+$ peak (assigned as allyl methacylate), with methacrylic acid observed as $C_4H_7O_2^+$ at *m/z* 87.0447 (+0.1 mmu error).

Several binary epoxy formulations (separate resin and hardener) were examined. Figures 4 and 5 show the spectrum of two separate uncured components of a fast-curing epoxy and Figure 6 shows the cured epoxy.

The major compound in the uncured epoxy resin (black component) is identified by exact mass as the diglycidyl ether of bisphenol A or DGEBA. This has the composition $C_{21}H_{24}O_4$ with $[M+NH_4]^+$ observed at *m/z* 358.2018. Fragments are seen at *m/z* 191.1072 ($C_{12}H_{15}O_2^+$) and *m/z* 325.143982 ($C_{20}H_{21}O_4^+$) . The major component in the hardener is identified as tris (2,4,6-dimethylaminomethyl) phenol ("DMP"), a widely used epoxy accelerator, with abundant fragments at nominal *m/z* 164.1075 ($C_{10}H_{14}NO^+$) and 221.165388 ($C_{13}H_{21}N_2O^+$). Peaks corresponding to DGEBA and the accelerant are evident in the cured epoxy resin.

A variety of other glues, cements, and adhesives were examined. Each showed a characteristic pattern, permitting the identification of the material. Residual solvent, residual monomer, unreacted and partially reacted components were detected together with pyrolysis fragments.

Conclusion

DART can be applied to the direct identification of adhesives and resins on surfaces. Exact mass measurements coupled with accurate isotopic abundances aid in the assignment of components in the adhesive formulations.