The AccuTOF™-DART® 4G: The Ambient Ionization Toolbox™

Introduction
JEOL introduced the AccuTOF-DART in 2005 as the first commercially available ambient ionization mass spectrometer system. The atmospheric pressure ionization interface (API) for the AccuTOF system, originally designed as a simple, rugged and reliable LC/MS interface, became the ideal platform for developing the Direct Analysis in Real Time (DART) ion source. Because the DART ion source can be positioned directly in front of the AccuTOF sampling orifice without additional interface hardware, a variety of ambient ionization techniques are available to the AccuTOF-DART operator without removing the DART ion source. The third-generation AccuTOF-DART 4G system is an “ambient ionization toolbox” that allows the analyst to choose ionization methods that are best matched to the samples to be analyzed.

DART
The DART ion source can be operated on the AccuTOF-DART 4G in several different modes to provide complementary information about substances to be analyzed.

Helium DART: moderately polar small molecules
In positive-ion mode, helium DART\(^1\) generally produces protonated molecules \([M + H]^+\) for compounds with a basic site, a heteroatom, or a site of unsaturation. In negative-ion mode, helium DART produces deprotonated molecules \([M – H]^–\) for compounds such as carboxylic acids or phenols that have a labile proton. Samples are introduced directly into the DART gas stream. By heating the helium gas, DART can detect volatile and semi-volatile compounds. Compounds with a molecular weight below 1000 can generally be detected by helium DART. Some compounds with molecular weights in excess of 2000 can be detected if they are sufficiently volatile.

Figure 1. Positive-ion helium DART mass spectrum showing additives in a synthetic motor oil.
**O\textsubscript{2}**\textsuperscript{−} attachment: nonpolar molecules (alkanes, alcohols)

Some compounds, including saturated alkanes and alcohols do not readily undergo proton transfer reactions. These compounds can be analyzed with the DART ion source by forming adducts with oxygen anions\([2]\). For this experiment, samples in solution are aspirated directly into the sampling orifice of the AccuTOF atmospheric pressure interface while the DART is operated in negative-ion mode as a source of O\textsubscript{2}. Rapid expansion into vacuum cools the weakly bound [M + O\textsubscript{2}]\textsuperscript{−} species for detection by the AccuTOF.

![Compounds detected as \([M + O\textsubscript{2}]\textsuperscript{−}\)](image)

**Figure 2. Negative-ion O\textsubscript{2}**\textsuperscript{−} attachment DART mass spectrum of the motor oil from Figure 1, showing the base oil components including C24-C44 alkanes and an alkynaphthalene.

**Dopant-assisted argon DART: molecular ions and proton transfer**

Argon DART is more selective than helium. Because the internal energy of Ar\textsuperscript{+} is 11.55 eV, water is not ionized. Only compounds with a low ionization energy are detected. Charge transfer or proton transfer reactions can be induced by adding a dopant such as acetone, methanol, toluene, fluorobenzene or chlorobenzene\([3, 4]\). Dopant-assisted argon DART can complement helium DART by producing molecular ions for compounds such as polynuclear aromatic hydrocarbons (PAHs), and may reduce fragmentation and enhance protonation for labile compounds.

![Figure 3. Argon DART mass spectrum showing molecular ions for lycopene and other compounds in a hexane extract of ketchup.](image)
**Pyrolysis DART: industrial materials, polymers**

Although high-molecular-weight materials such as industrial polymers cannot be detected intact by DART, increasing the DART heater to 350°C or higher can result in degradation to produce characteristic “fingerprint” fragments.

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**Figure 4. “Pyrolysis DART” mass spectra of three polymers obtained with helium gas and the DART gas heater set to 350°C.**

- **Styrene/isoprene ABA**
- **Nylon 6**
- **PVC**

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**Note: Thermal desorption/pyrolysis DART: even better for materials and polymers**

A thermal desorption/pyrolysis stage (The Biochromato, Inc. “IonRocket”) is designed for use with DART. Highly reproducible thermal desorption profiles show outgassing, additives, and high-quality pyrolysis DART mass spectra for materials. Thermal desorption/pyrolysis analysis of duct tapes and fibers is discussed in separate application notes.
Inlet ionization: Polar molecules including peptides and medium-sized proteins
Inlet ionization\(^5\) complements DART by allowing the operator to analyze polar and charged compounds. The sample can be aspirated directly from solution into orifice 1, or a matrix (3-nitrobenzonitrile) can be added to induce ionization.

![Figure 5: Solvent-assisted inlet ionization of naphthol blue black dye.](image)

FilterSpray\(^6\): Polar molecules and elemental analysis
FilterSpray\(^6\) allows you to spot a sample on a disposable paper triangle and to obtain electrospray ionization mass spectra without the complication of pumps or plumbing. FilterSpray can even be used for ambient inorganic analysis\(^7\). A FilterSpray attachment can be mounted onto the linear rail of the AccuTOF-DART to permit FilterSpray analysis on the sample platform as DART without any hardware modifications.

![Figure 6. FilterSpray analysis shows Pb and Cr from lead chromate pigment on a 1948 "Gold Star Mothers" postage stamp.](image)
Conclusion

The AccuTOF-DART provides a versatile platform for ambient ionization mass spectrometry. A wide range of ambient ionization methods can be carried out without removing the DART ion source. This provides the chemist with complementary techniques to analyze a wide variety of chemical compounds and materials.

References


