

## The AccuTOF® Atmospheric Pressure Interface: an Ideal Configuration for DART® and Ambient Ionization

### Introduction

The DART ion source was developed on the JEOL AccuTOF time-of-flight mass spectrometer which allows the exit of the DART source to be positioned within millimeters of the sampling orifice (orifice 1) of the mass spectrometer atmospheric pressure interface (API). The AccuTOF vacuum system is robust, highly resistant to contamination, and capable of pumping helium DART gas without assistance.

### The AccuTOF API

Figure 1 shows a schematic diagram of the AccuTOF atmospheric pressure interface. The API consists of two off-axis skimmers (designated "orifice 1" and "orifice 2") with an intermediate ring lens, followed by a bent RF ion guide. The off-axis skimmer design traps contamination -- ions are electrostatically guided upward toward orifice 2 whereas neutral molecules are pumped downward. Any contamination that enters the API is either pumped away into the rough pump (RP) or trapped on the lower part of orifice 2. The bent RF ion guide provides an additional level of protection. This makes the AccuTOF an ideal mass spectrometer for DART analysis of dirty "real-world" samples such as mud, biological fluids, melted chocolate, polymers, and even crude oil. In addition, orifice 1 is easily accessible and is operated at low voltage and current, making it a convenient platform for ambient ionization sources.

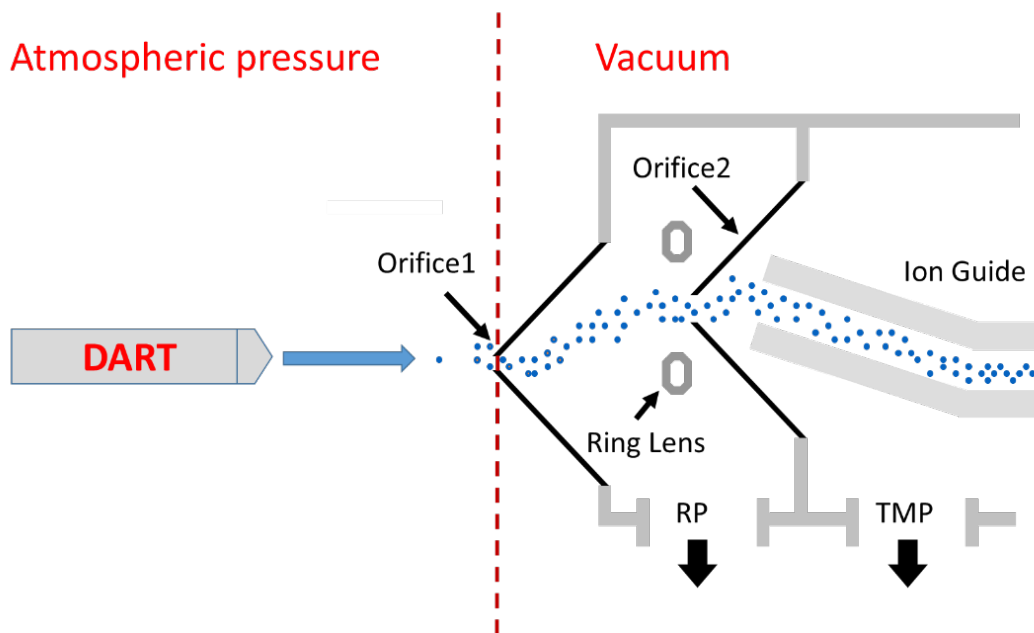


Figure 1. Schematic diagram of the AccuTOF atmospheric pressure interface (API)

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DART® is a registered trademark of JEOL USA, Inc. (Peabody, MA USA)

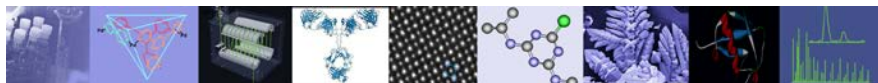


Figure 2 shows the DART source mounted on the AccuTOF with the exit of the ceramic insulator positioned approximately 1 cm from the apex of orifice 1. This is the optimal positioning of the DART source for normal operation.

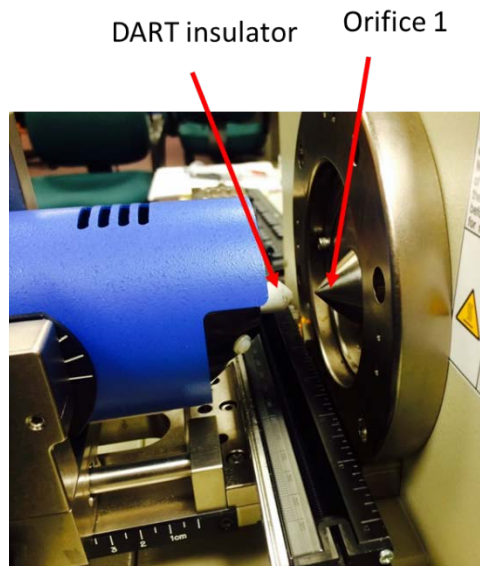


Figure 2. The white DART ceramic insulator cap is positioned approximately 1 cm from the apex of orifice 1 (the silver cone on the right).

## The Vapur® Interface

### Description

The vacuum systems of other mass spectrometer systems are not capable of handling the additional pumping burden and may shut down if the DART is operated with helium. The Vapur® interface allows the DART source to be used with non-JEOL mass spectrometers. It consists of a ceramic tube mounted on a custom flange and an auxiliary pumping stage (Figure 3 and Figure 4) that is used as an interface for mounting the DART on ALL non-JEOL mass spectrometers and for mounting certain DART accessories that require additional clearance.

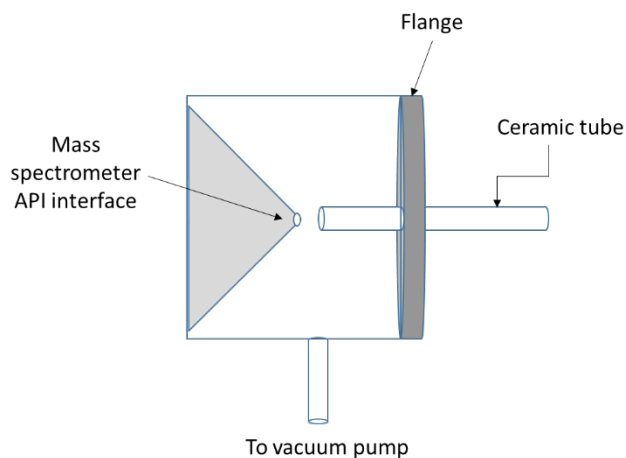


Figure 3. Schematic diagram of Vapur interface. On the AccuTOF, the gap between orifice 1 and the exit of the Vapur ceramic tube should be 2 mm for optimal performance.

Vapur® is a registered trademark of IonSense LLC (Saugus, MA USA)

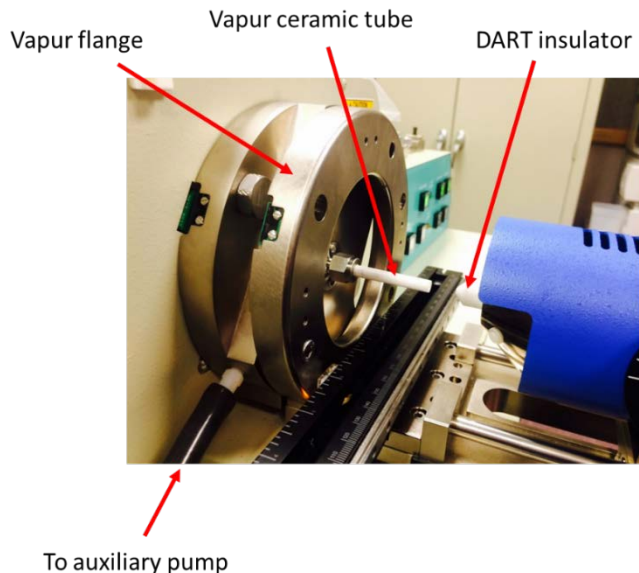
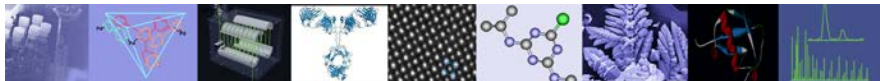


Figure 4. The Vapur interface mounted on the AccuTOF DART.

**Loss of signal**

The large diameter of the Vapur interface’s ceramic tube improves reproducibility for some analyses by reducing gas turbulence and it provides space for mounting some accessories such as the IonSense 3+D Scanner. However, increasing the gas flow path increases the likelihood of ion-molecule reactions occurring, which can cause a loss of signal for samples that do not have a high proton affinity. Figure 5a shows the normal DART positive-ion low-mass background without the Vapur installed. The dominant reagent ions are protonated water and proton-bound water dimer. Figure 5b shows the background measured with the Vapur installed. Protonated water is barely visible, even at a magnification of 25X. The other peaks are trace impurities in the gas lines and in the background that have a higher proton affinity than water.

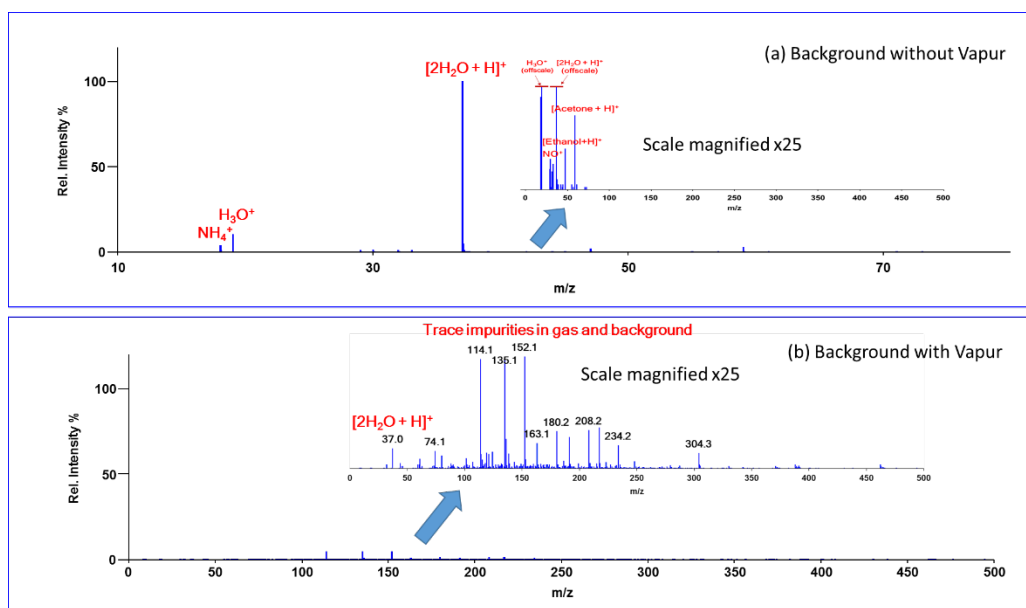
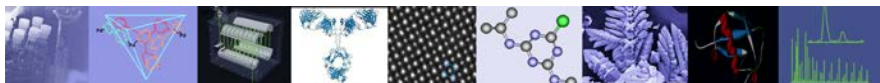


Figure 5. (a) positive-ion low-mass DART background without the Vapur installed, showing the dominant reagent ions with trace laboratory solvent peaks and (b) the low-mass background observed with the Vapur installed.



Nonpolar compounds are particularly susceptible to signal loss due to ion-molecule reactions at atmospheric pressure. Figure 6 illustrates the signal loss for a roughly equimolar mixture of epitestosterone and quinine with trace levels of methyl stearate as the Vapur is installed. The methyl stearate signal is completely lost, epitestosterone's signal reduced by a factor of 6, and even the relatively polar quinine is attenuated by a factor of 2.

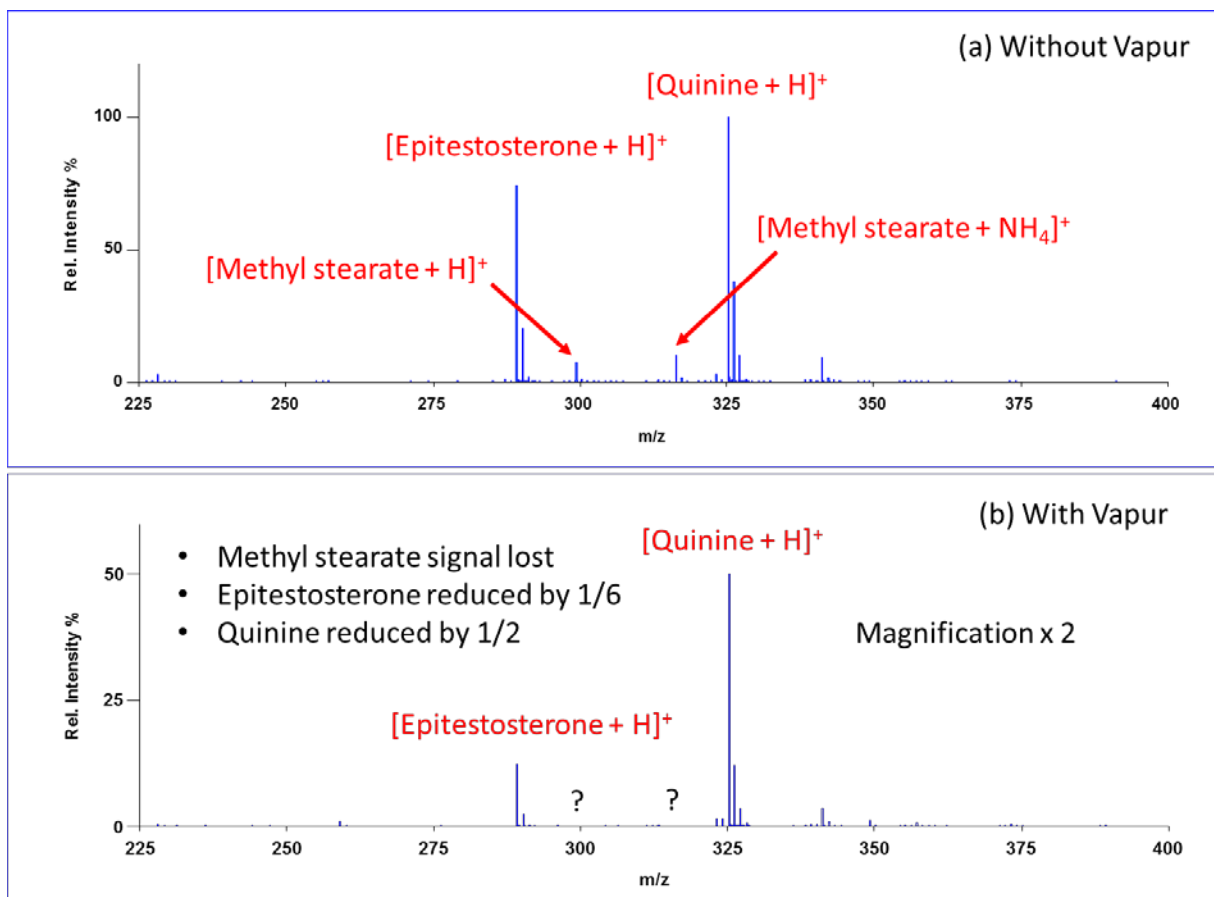


Figure 6. Comparison of signal for quinine, epitestosterone, and methyl stearate (a) without the Vapur interface and (b) with the Vapur interface.

### Differences in ionization chemistry

Samples such as ethers and carbonyls measured with the Vapur interface installed tend to form ammonium adducts preferentially. This results from ion-molecule reactions occurring during sample transport through the Vapur, which favor ammonium over hydronium due to the high proton affinity of trace atmospheric ammonia. Samples without a strongly basic site that normally produce proton adducts by DART without the Vapur may be observed as ammonium adducts if the Vapur is installed. Figure 7 shows the comparison of the DART mass spectra measured for a polyethylene glycol (PEG) sample measured without the Vapur (Figure 7a) and with the Vapur (Figure 7b). Proton and ammonium adducts are observed in both spectra, but the proton adducts dominate in Figure 7a, whereas ammonium adducts dominate in Figure 7b.

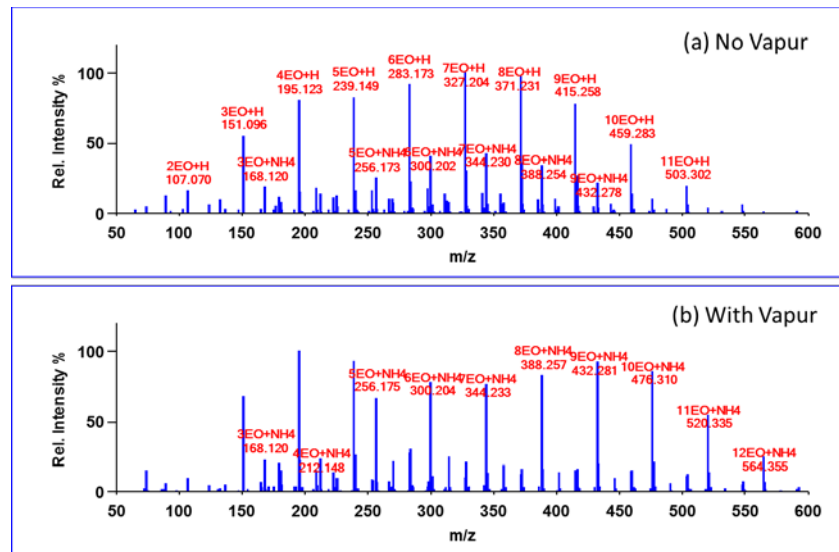
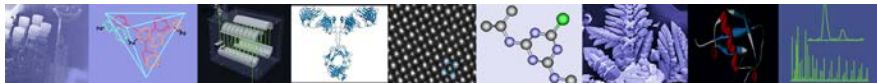


Figure 7. Positive-ion DART mass spectra of a PEG sample measured (a) with no Vapor and (b) with the Vapor installed.

### Sample Carryover

Sample carryover in the Vapor is a problem for some samples. Therefore it is important to limit sample quantity when using the Vapor and to check for cross-contamination between samples. Figure 8 shows an example for the analysis of a sample containing 1% diisobutyl phthalate in isopropanol. Samples were introduced by depositing them onto the sealed end of a melting point tube and positioning the tube in the DART gas stream for several seconds. Three replicate measurements were made for the sample, followed by a mass reference standard (Jeffamine<sup>®</sup> M-600, Huntsman Corporation). Figure 8a shows the results of the sample measurement without the Vapor installed, and Figure 8b shows the results of the same measurements with the Vapor installed. The red arrows indicate the time at which each sample was introduced into the DART gas stream. Note that the total ion current and reconstructed ion current chromatogram (RIC) for diisobutyl phthalate show increasing contamination in Figure 8b as the DIBP is adsorbed onto the ceramic tube. The results obtained without the Vapor do not show any sample carryover and it is easy to determine when each sample was measured.

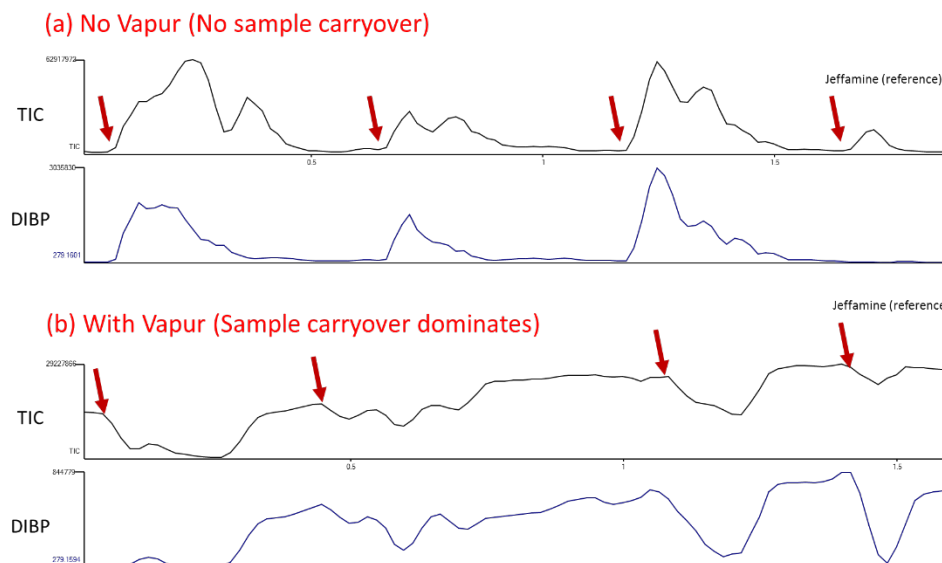
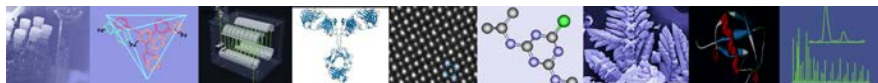


Figure 8. Chromatograms for three replicate measurements of a sample containing diisobutyl phthalate (DIBP) (a) with no Vapor and (b) with the Vapor installed.



## Vapur Summary

- Features
  - Assists weaker vacuum systems to pump helium.
  - Improves reproducibility by reducing effects of turbulence
  - Provides a universal DART interface.
- Problems
  - Required for DART on ALL mass spectrometers EXCEPT THE JEOL AccuTOF.
  - Ion-molecule reactions occur as ions are transported over a longer distance
  - Loss of non-polar and reactive compounds including the air peaks
  - Ammonium adducts dominate over  $MH^+$
  - Increased oxidation
  - Problems with sample carryover if compounds stick to the Vapur ceramic tube.
  - Requires an extra vacuum pump

## Conclusion

The AccuTOF mass spectrometer atmospheric pressure interface is an ideal platform for use with the DART and ambient ionization sources. It permits the use of the DART without additional pumps, interfaces, or hardware that can cause sample carryover, loss of signal, or changes in the DART ionization chemistry.