Detection of Lipids Using Direct Analysis in Real Time Mass Spectrometry

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AIM

To show that DART™ (Direct Analysis in Real Time) mass spectrometry can quickly provide mass spectral information for a wide variety of samples containing lipids with minimal sample preparation.

INTRODUCTION

There has been a recent trend in mass spectrometry towards the development of "open-air" ionization sources. These techniques allow for the rapid analysis of samples at atmospheric pressure with little or no sample preparation. The Direct Analysis in Real Time (**DART™**) ion source, which is ideal for the analysis of small molecules, represents the first and simplest of the open-air techniques.[1] This source creates ions based on the interactions of long-lived excited state neutral atoms or molecules ("metastables") with the sample and atmospheric gases. **Figure 1** shows a schematic of the DART™ source. Samples are typically placed in a stream of helium or nitrogen containing these metastables (sample gap in Figure 1), which results in the formation of ions that are introduced into the mass spectrometer vacuum system through an orifice. Different ionization mechanisms occur depending on the type of sample being analyzed (and its concentration), the nature of the carrier gas used, and the polarity of the ions formed. A complete discussion of these mechanisms can be found elsewhere.[2]

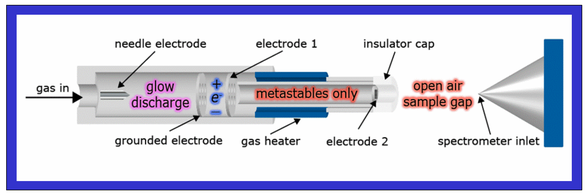

Figure 1. Schematic of the DART™ ionization source.

When the DART™ is installed on a JEOL AccuTOF™ high resolution mass spectrometer (**Figure 2**), the robustness of the atmospheric pressure interface makes the overall system remarkably resistant to contamination. As a result, it is possible to directly analyze samples such as cooking oils, peanut butter, chocolate bars, and biodiesel without sample cross contamination. Moreover, these samples produce simple mass spectra consisting of $M^{+\bullet}$ and protonated molecules $[M+H]^+$ in positive ion mode and deprotonated molecules $[M-H]^-$ in negative ion mode. Additionally, the AccuTOF provides exact mass measurements and accurate isotopic abundances that can in turn be used to determine the elemental composition of the sample. Consequently, AccuTOF-DART™ can quickly provide answers and insight for a broad spectrum of analytical questions.

Figure 2. An AccuTOF-DART™ system.

METHODS

A DART™ ionization source (IonSense, Saugus, MA) was interfaced to a JEOL AccuTOF™ time of flight mass spectrometer (**Figure 2**). Analysis by AccuTOF-DART™ was done by placing the sample in the ionizing gas stream for a few seconds and recording the mass spectra. For liquids, the closed end of a melting point tube was dipped into the sample and immediately placed in the DART™ stream (See **Figure 3**). For solids, the sample was positioned into the DART™ stream using tweezers. A mass spectrum of poly(ethylene glycol) with an average molecular weight of 600 or 1000 was included in each data file as a reference standard for exact mass measurements. All compounds were confirmed through exact mass measurements and isotope pattern matching.

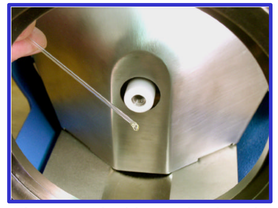

Figure 3. Liquid sample placed in DART™ stream.

RESULTS AND DISCUSSION

AccuTOF-DART™ has many applications towards the analysis of oils, fats, and surfactants. One area this technology can be applied involves directly analyzing different cooking oils for their triglyceride content. **Figure 4** shows that these compounds are readily detected by the AccuTOF-DART™ system. Additionally, this data shows that triolein (OOO) is the major component in olive oil while increasing unsaturation is observed for the Canola/safflower oil blend and sesame oil. Additionally, fatty acid composition can be characterized indirectly by the unsaturation profile of the triglycerides and directly by examining the fatty acids released when the oil is exposed to an elevated DART™ gas temperature (**Figure 5**). Another DART™ application involves the direct analysis of an oily stain on a previously washed shirt. The mass spectrum of the stained region (**Figure 6**) shows a distinctive pattern of saturated fatty acids and their proton bound dimers, monoglycerides, and triethanolamine (TEA). Also, the direct analysis of corn biodiesel (**Figure 7**) shows a variety of saturated and unsaturated fatty acid methyl esters (FAMES). **Figure 8** shows the DART™ analysis of a cooked sunflower seed, which showed the presence of Vitamin E.

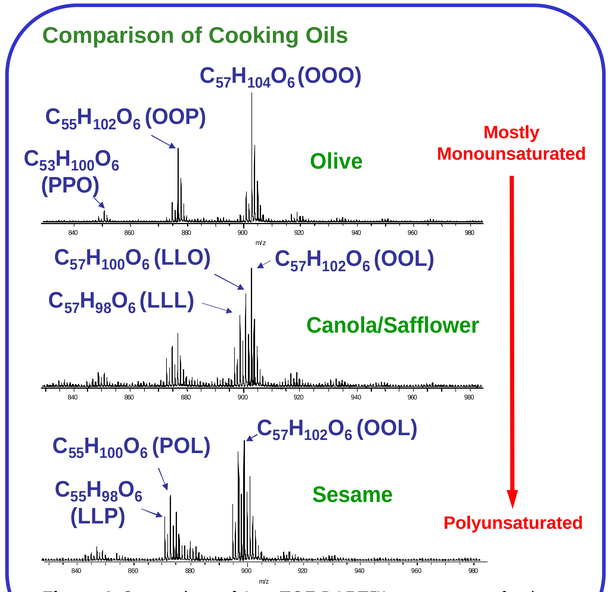

Figure 4. Comparison of AccuTOF-DART™ mass spectra for the triglyceride content in 3 different cooking oils.

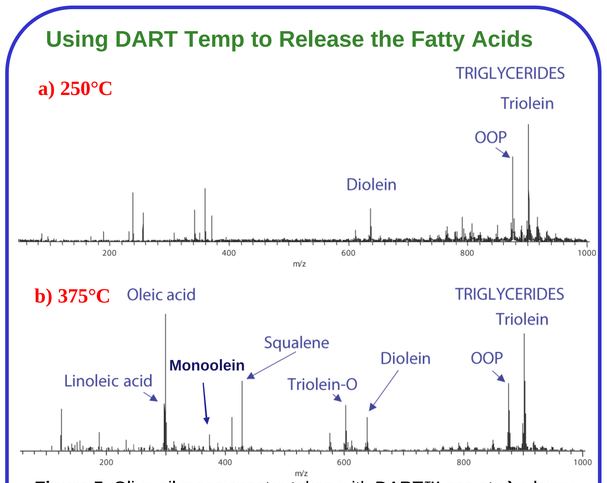

Figure 5. Olive oil mass spectra taken with DART™ gas at **a)** a lower temperature of 250°C and **b)** a higher temperature of 375°C which released the free fatty acids. O, oleic; P, palmitic.

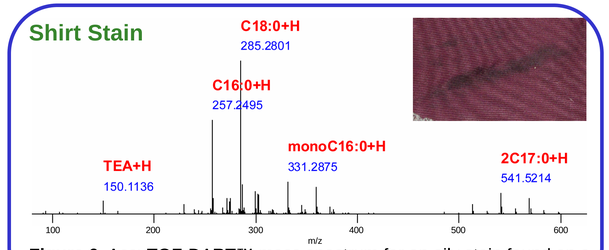

Figure 6. AccuTOF-DART™ mass spectrum for an oily stain found on a freshly laundered shirt.

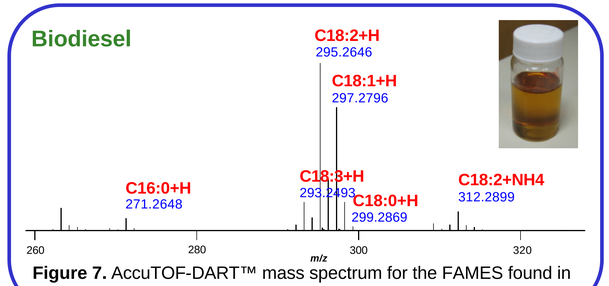

Figure 7. AccuTOF-DART™ mass spectrum for the FAMES found in corn biodiesel.

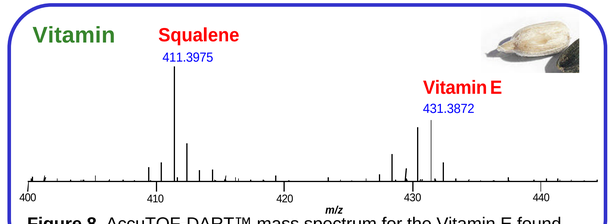

Figure 8. AccuTOF-DART™ mass spectrum for the Vitamin E found during the analysis of a de-hulled sunflower seed.

CONCLUSIONS

•AccuTOF-DART™ can be used to quickly provide information about lipids in a wide variety of samples with minimal to no sample preparation.

REFERENCES

[1] Cody, R. B.; Laramee, J. A., "Method for atmospheric pressure ionization" US Patent Number 6,949,741 issued September 27, 2005. Priority date: **April 2003**.

[2] Cody, R.B., J.A. Laramée, and H.D. Durst, "Versatile New Ion Source for the Analysis of Materials in Open Air under Ambient Conditions." *Anal. Chem.*, **2005**. 77(8): p. 2297-2302.

ACKNOWLEDGEMENTS

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