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Real-Time Analysis of Flavors Using DART and the ACQUITY QDa Mass Detector

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APPLICATION BENEFITS

- Direct analysis of food flavors using mass spectrometry detection
- Real-time screening of volatile and semi-volatile compounds
- Little to no sample preparation
- No chromatography required
- Ease of use

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ACQUITY® QDa® Detector

MassLynx® MS Software

KEYWORDS

Flavors, aroma, volatiles, food QC, food authenticity, tobacco, DART, mass detection, ambient ionization

INTRODUCTION

Characterization of flavors in food products is critical for a consumer's perception of aroma and taste, food quality, and product branding. Maintaining consistent flavor in food products requires quality control testing to ensure the right flavor is applied to the product at the right levels and that the product is free from contamination and off-odors.

Analysis of flavor compounds is challenging and time consuming as it requires several lab-based measurements. Based on the flavor source (e.g. natural versus synthetic), flavor formulations can contain several hundred compounds of varying solubility, volatility, concentrations, and stability. A combination of gas chromatography (GC) and liquid chromatography (LC) based methods integrated with mass spectrometry (MS) are typically applied for the identification and quantification of food flavors. These procedures require isolation and concentration of flavor compounds from their food matrix prior to instrument analysis.

This application note demonstrates the utility of DART (direct analysis in real time) and ACQUITY QDa mass detection for rapid, accurate, and cost-effective flavor characterization, for monitoring product quality, and reducing production costs. DART-MS was applied to characterize volatile and semi-volatile flavors in whiskey, chewing gum, and tobacco samples with different characteristic flavors. The flexibility of sample introduction using an ambient ionization technique like DART combined with the sensitivity of the ACQUITY QDa Detector reduce analysis times, and increases confidence in results compared to conventional methods, making this system more suitable for quality control applications in the food, beverage, and consumer goods industries.[1-3]

EXPERIMENTAL

DART method	Whiskey	Gum	Tobacco
Ion mode	Positive	Positive	Positive
Run temp. (°C)	350	450	450
Sampling speed (mm/sec)	0.5	NA	NA
Exit grid voltage (V)	350	350	350
QDa method	**Whiskey**	**Gum**	**Tobacco**
Ion mode	+	+	+
Cone voltage (V)	10	5	5
Mass range (amu)	50 to 500	50 to 500	50 to 500
Sampling frequency (Hz)	2	2	2

Table 1. DART and mass detection method parameters used to acquire data for whiskey, chewing gums, and tobacco samples.

Sample analysis

Whiskey, chewing gum, and chewing tobacco samples were purchased commercially. No sample preparation was performed on the samples prior to analysis with the DART-MS system. Three different sampling techniques were used for the sample types (Figures 1A–1C). Chewing gum with four different flavors (original mint, spearmint, tropical twist, and cinnamon) were evaluated in this study. The chewing gum was sampled as a solid by holding a piece of gum with tweezers in the path of the heated ionizing helium beam generated by the DART source (Figure 1A). Whiskey samples (Scotch, Bourbon, Canadian, and Irish) were sampled as liquids by spotting 5 µL of whiskey onto Quickstrip cards that were moved through the helium beam in an automated fashion (Figure 1B). Chewing tobacco samples with four different flavors (Natural, Classic Mint, Classic Straight, and Classic Wintergreen) were investigated by DART-MS. The aroma sampling (Figure 1C) of chewing tobacco was performed by analyzing the volatiles in the headspace above the sample. In this case, the open chewing tobacco can was placed directly underneath the flow of the helium beam.

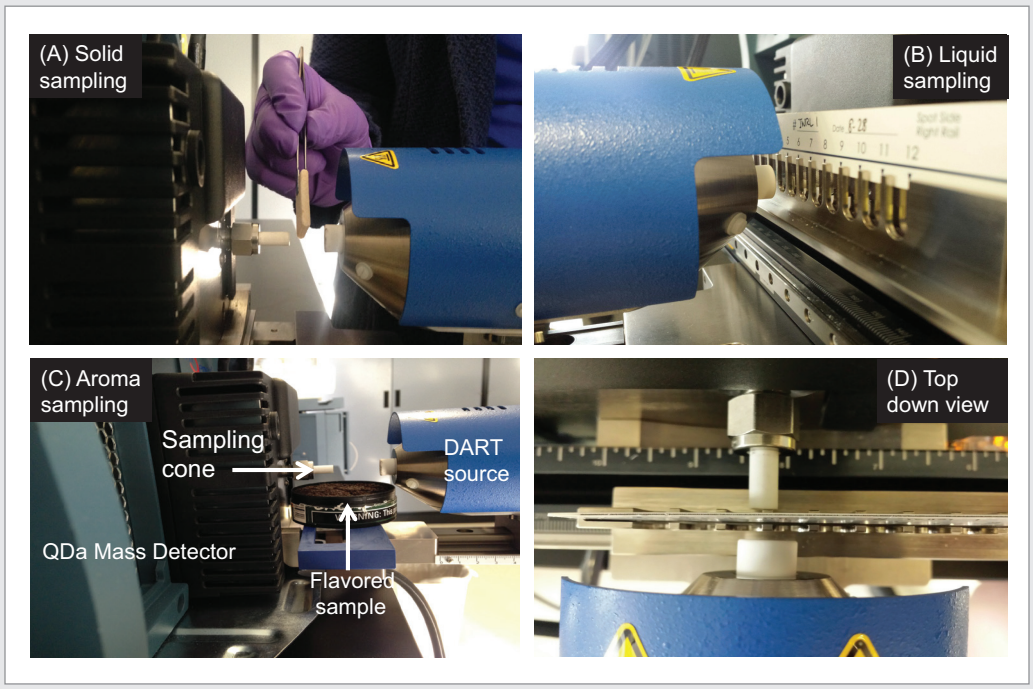

Figure 1. DART-MS sampling options: (A) Solid sampling; (B) Liquid sampling using Quickstrip; (C) Aroma sampling; and (D) Top-down view of the ceramic tube pulling ions into the ACQUITY QDa source.

RESULTS AND DISCUSSION

METHOD DEVELOPMENT AND OPTIMIZATION

For operating DART and the ACQUITY QDa, a few important parameters must be optimized for each sample type analyzed, including cone voltage and DART sampling temperature. When optimizing the cone voltage, it must be decided whether to use a low cone voltage (~5 to 10 V), or a high cone voltage (~30 V). Using a high cone voltage can induce fragmentation of the compounds which can be beneficial for generating unique mass profiles of the samples. The effects of high and low cone voltages are demonstrated in the whiskey samples shown in Figure 2.

Sampling temperature is also a very important parameter that must be optimized for each sample type. Compound desorption and ionization efficiency are dependent on this parameter. Figure 3 shows the mass spectra collected from the same whiskey samples at four different temperatures. Some ions are only present at certain temperatures while the intensities of the other ions vary dependent upon temperature.

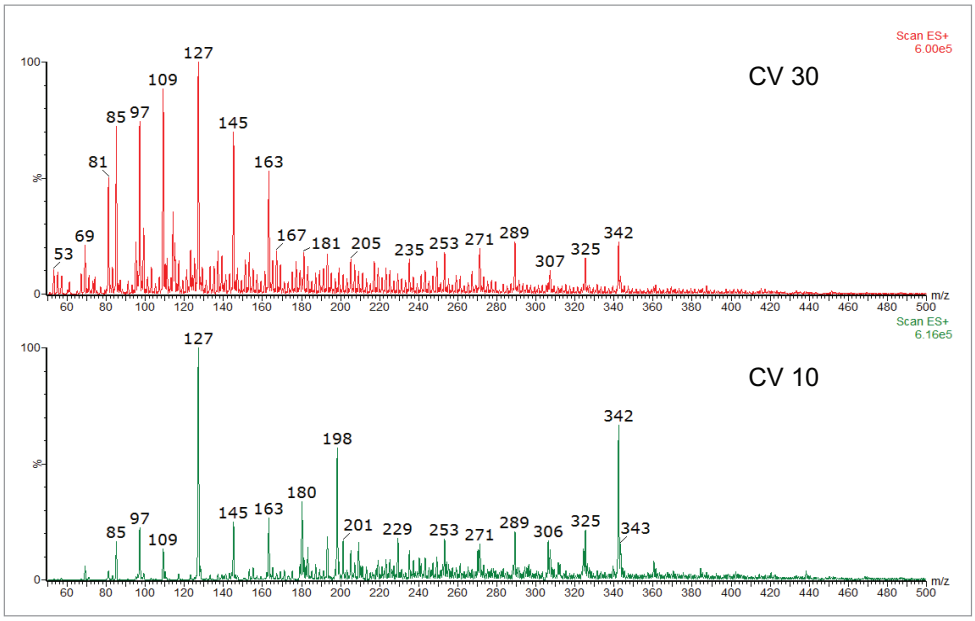

Figure 2. Mass spectrum of whiskey sampled at a cone voltage of (top) 30 V and (bottom) 10 V.

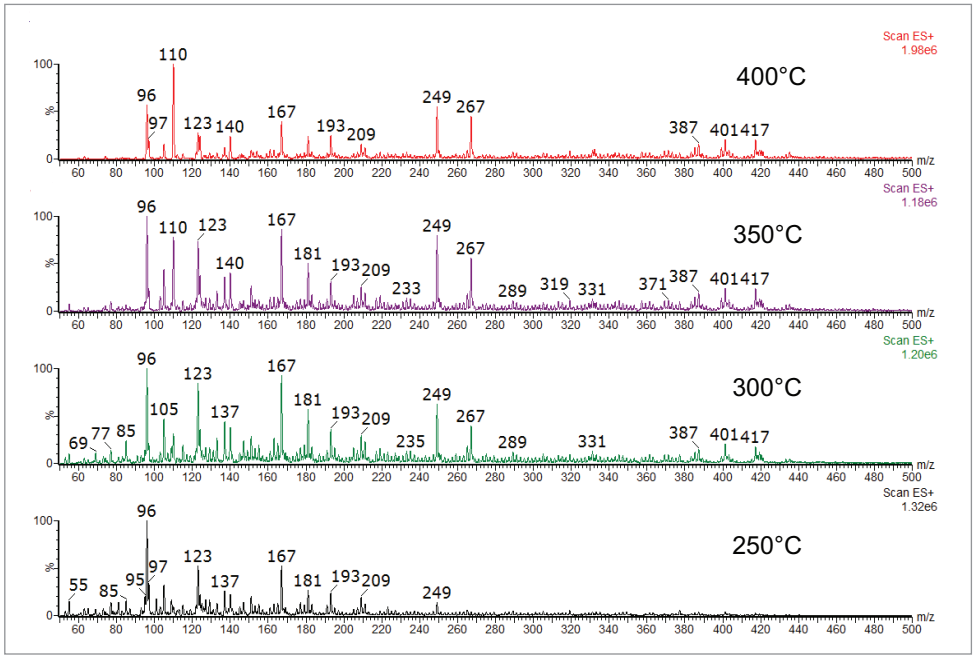

Figure 3. Whiskey mass profiles at different sampling temperatures ranging from (top) 400 °C to (bottom) 250 °C.

WHISKEY ANALYSIS

Different brands of whiskey were tested using optimized DART-MS conditions. Whiskey flavor is heavily influenced by the fermentation and aging process during production. Grain type, barrel type/char, and length of aging all contribute to making each brand distinct. Figure 4 demonstrates the unique fingerprint generated by DART-MS for four different brands of whiskey. Some ions are common among a few of the samples (*m/z* 342, 198, 127, 97), but vary by relative intensity and ratio. Other ions are unique to one particular sample type (*m/z* 209 and 249 in bourbon). The bourbon sample has the most unique flavor profile of the four whiskey samples.

The nominal mass was used for tentative identifications of some of these ions for characterizing the flavor profiles. The bourbon sample contained a very significant peak at *m/z* 209, that may be attributed to sinapaldehyde, a breakdown product of lignin resulting from the wooden aging barrel. The Scotch blend, Canadian, and Irish whiskies all contain an ion at *m/z* of 145. This ion could be attributed to ethyl hexanoate, which imparts a fruity odor. This DART-MS analysis method cannot be used to identify and confirm unknown flavor compounds, but it can be used as a tool to rapidly identify differences between samples and sample types. To confirm the flavor identifications indicated in the DART-MS data, reference flavor standards and conventional methods for flavor analysis should be used.

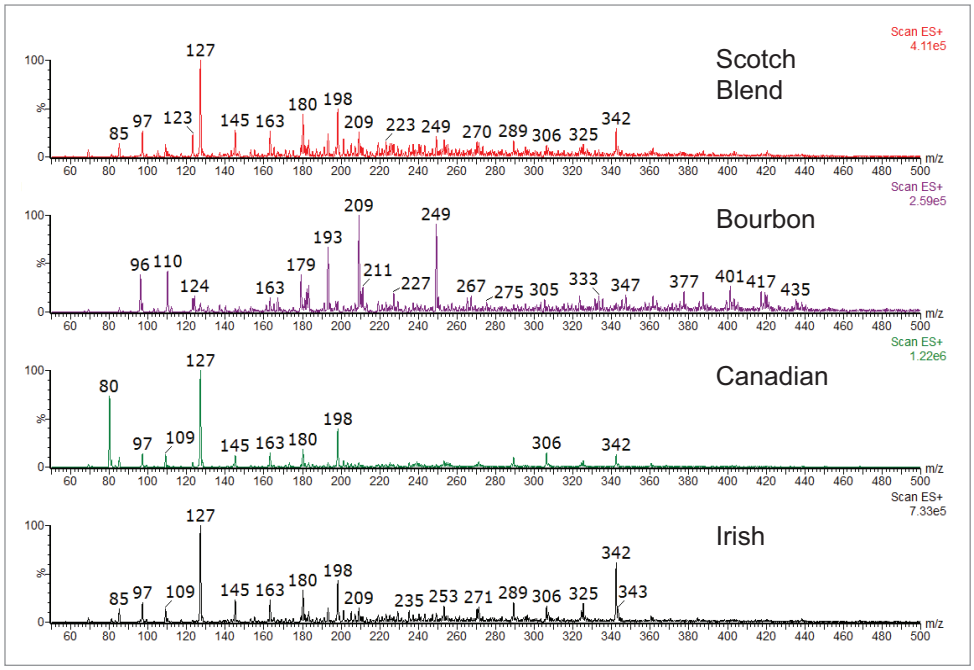

Figure 4. Mass spectral profile of four different brands of whiskey analyzed using DART-MS.

CHEWING GUM ANALYSIS

The addition of the proper flavors and sweeteners to the gum base is a critical step in the manufacturing of high quality chewing gums with long lasting flavor. Original mint, spearmint, tropical fruit, and cinnamon are the most preferred flavors by consumers today. These four flavored chewing gums of the same brand were directly analyzed by holding the gum samples in between the DART source and the ACQUITY QDa inlet.

As observed in Figure 5, DART-MS generated a unique mass spectral fingerprint for the four different flavored chewing gum products. The peaks at *m/z* 159, 236, and 237 were common to all of the chewing gum samples and may be attributed to the gum matrix. The cinnamon mass profile shows the presence of its characteristic flavor ingredient, cinnamaldehyde (*m/z* 133). Ions 172, 212, and 270 represent cooling agents that are typically used in tropical fruit, spearmint, and original mint gums. The mass profile of spearmint flavored gum shows the presence of characteristic flavor, carvone (*m/z* 150). Methyl salicylate (*m/z* 153) was also observed in both the spearmint and original gum samples.

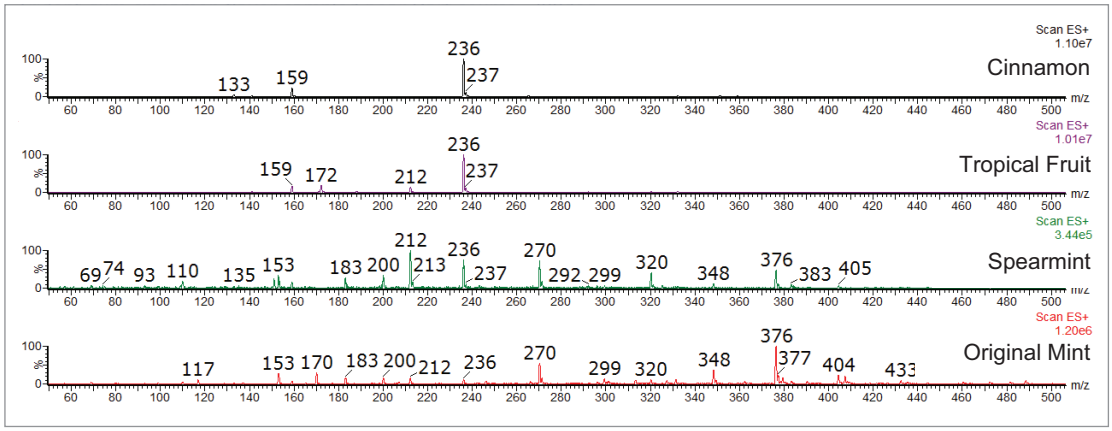

Figure 5. Mass spectral profile of four different flavors of chewing gum analyzed using DART-MS.

CHEWING TOBACCO ANALYSIS

Open tobacco cans were placed between the DART source and the ACQUITY QDa inlet for direct analysis of headspace volatiles. Figure 6 demonstrates the mass spectral fingerprint generated by DART-MS for wintergreen, straight, mint, and natural flavored smokeless tobacco products. The nicotine peak (*m/z* 163, protonated molecular ion) dominates the volatile headspace of these tobacco samples irrespective of the applied flavor. Nicotine is readily volatile at room temperature (vapor pressure 5.5 Pa at 25 °C) and is the base peak in the mass profiles. Ions with *m/z* 80, 86, 108, 132, 136, 276, and 325 were observed in all of the tobacco samples and may be attributed to the tobacco matrix.

Methyl salicylate (*m/z* 152) is the characterizing flavor of wintergreen and its protonated molecular ion (*m/z* 153) was observed in the mass profile of the wintergreen tobacco product. Ethyl salicylate (*m/z* 167, protonated molecular ion), a characteristic flavor ingredient was detected in the straight flavored tobacco samples. The mass profile of the mint tobacco sample showed trace levels of several flavor markers indicating the use of a natural source of peppermint oil including compounds such as limonene (*m/z* 137), menthone (*m/z* 155), traces of methyl salicylate (*m/z* 153), and ethyl salicylate (*m/z* 167). No major flavor markers were identified in the natural tobacco samples which has the simplest and relatively low intensity mass profile suggesting that not many flavors had been added to this product.

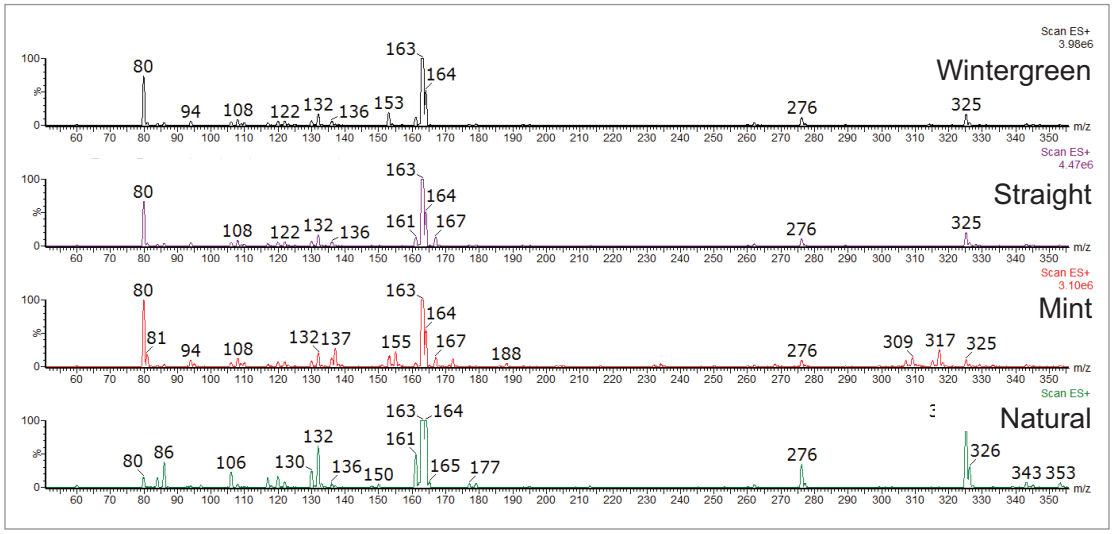

Figure 6. Mass spectral profile of four different flavors of chewing tobacco analyzed using DART-ACQUITY MS.

CONCLUSIONS

This application note demonstrates the utility of DART and ACQUITY QDa mass detection for rapid monitoring and cost effective fingerprinting of food flavors to determine product authenticity and for quality control. Three sample types were analyzed using three different sample introduction techniques for their flavor profiles. The mass spectral fingerprints for the different samples in each of the sample groups (whiskey, gum, and tobacco) were unique to each sample. For the whiskey samples, potential flavor components influencing the flavors of the types of whiskey sampled were detected. The gum and tobacco samples exhibited flavor components typically associated with the particular samples, such as methyl salicylate in spearmint flavored products.

The flexibility of sample introduction using an ambient ionization technique like DART combined with the ACQUITY QDa Mass Detector reduces overall analysis and decision making times in R&D and manufacturing QC environments. The elimination of the need for sample preparation also provides the benefit of having a system located in the R&D and QC labs for rapid monitoring and quality control applications in the food, beverage and consumer goods industries.

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