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Detection of Low Molecular Weight Adulterants in Beverages by Direct Analysis in Real Time Mass Spectrometry

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Abstract
Direct Analysis in Real Time Mass Spectrometry (DART-MS) has been used to detect the presence of non-narcotic adulterants in beverages. The non-narcotic adulterants that were examined in this work incorporated a number low molecular weight alcohols, acetone, ammonium hydroxide, and sodium hypochlorite. Analysis of the adulterants was completed by pipetting 1 µL deposits onto glass microcapillaries along with an appropriate dopant species followed by introduction into the DART gas stream. It was found that detection of these compounds in the complex matrices of common beverages (soda, energy drinks, etc.) was simplified through the use of a dopant species to allow for adduct formation with the desired compound(s) of interest. Other parameters that were investigated included DART gas stream temperature, in source collision induced dissociation, ion polarity, and DART needle voltage. Sensitivities of the technique were found to range from 0.001 % volume fraction to 0.1 % volume fraction, comparable to traditional analyses completed using headspace gas chromatography mass spectrometry (HS-GC/MS). Once a method was established using aqueous solutions, fifteen beverages were spiked with each of the nine adulterants, to simulate real world detection, and in nearly all cases the adulterant could be detected either in pure form, or complexed with the added dopant species. This technique provides a rapid way to directly analyze beverages believed to be contaminated with non-narcotic adulterants at sensitivities similar to or exceeding those of traditional confirmatory analyses.

Introduction
Adulteration of beverages is a concern in several different fields including forensics, food safety, and industrial quality control because it can occur at any point from the time of manufacturing (where a manufacturer may knowingly or unknowingly contaminate a product), until the time of consumption (as may be encountered in forensic cases). Depending on the degree of adulteration, the introduction of unknown and potentially unsafe compounds into beverages can cause a number of dangerous side effects including poisoning or death. Therefore, it is important to have a method that is able to detect these compounds in the complex matrices of beverages rapidly, efficiently, and effectively. This paper aims to demonstrate how one such technique, direct analysis in real time mass spectrometry (DART-MS) can be used to complete this type of screening in a high throughput fashion.

DART-MS is a technique that has been applied to many areas of forensic analysis and quality control. It has been shown to be a viable tool in screening for a number of compounds ranging from explosives and narcotics to phthalates and pesticides. The major benefit of DART-MS is that the sample can be directly interrogated, removing the need of extensive sample preparation or chromatographic separation. Briefly, the DART source allows for sample analysis by using a stream of heated metastable gas molecules to desorb and ionize molecules off of a surface and into the vapor phase. Since there is no chromatographic element to the technique, analysis time is on the order of seconds, allowing for rapid screening. However, because the sample is directly introduced into the mass spectrometer without separation, competitive ionization and peak overlap can be concerns when complex matrices are analyzed.

This paper focuses on nine low molecular weight adulterants. These adulterants are common industrial and/or consumer chemicals, not narcotics like gamma-hydroxybutyric acid (GHB). These chemicals included: methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, acetone, ethylene glycol, ammonium hydroxide, and sodium hypochlorite. Methanol, a common laboratory solvent and component in windshield washer fluid, can be used to adulterate wines to give them a more bitter taste. 1-Propanol, a component of brake fluid and antiseptics, has been
used to adulterate vegetable oils and alcoholic beverages.\textsuperscript{9} Isopropanol (2-propanol), similarly, is a common antiseptic found in most hand sanitizer products. 1-Butanol is a widely used industrial solvent, a component of hydraulic fluid, and a component of paint thinner. Acetone, a constituent of nail polish remover and superglue, can also be used as a food additive. Ethylene glycol is a major component of radiator fluid, while ammonium hydroxide and sodium hypochlorite (the active component of bleach) are common household cleaners and have been used to adulterate beverages.

Detection of these compounds has been completed in the past using a number of different techniques. GC/MS has been used for detection of alcohols, acetone, and ethylene glycol in a number of different applications.\textsuperscript{6,7} While this technique is selective and specific, it requires an analysis time of minutes, as well as sampling the headspace of aqueous components, not the liquid itself. Liquid chromatography has also been used to detect these types of compounds, with the added benefit of being able to directly analyze aqueous solutions but with analysis times similar to GC/MS.\textsuperscript{10} Hypochlorite has been analyzed using GC coupled to flame ionization detection, but requires derivatization and sample runs on the order of minutes.\textsuperscript{11} A number of other techniques, including liquid chromatography, have been explored.\textsuperscript{12–14} Prior work focusing on the detection of alcohols by DART-MS proved it was possible with sample derivatization.\textsuperscript{15} This work highlights the ability of DART-MS to analyze these potential adulterants without derivatization as both neat samples, and in the complex solutions of common beverages. First, a series of parameters were evaluated to understand the conditions necessary for optimal adulterant detection. These parameters included gas stream temperature, ion polarity, and fragmentation voltage. Once a method was developed, limits of detection of both neat samples and spiked beverages were determined. Increased sensitivity and selectivity in complex matrices was aided by promoting adduct formation with the addition of a dopant material to the sampling rod and are discussed in detail.

**Materials and Methods**

**Solvents, Standards, & Sampling Material**

Methanol, 1-propanol, and acetone were purchased from Fisher Scientific\textsuperscript{®} (Waltham, MA, USA) as LC/MS grade solvents or better. 2-Propanol, 1-butanol, and ethylene glycol were purchased from Sigma-Aldrich as LC/MS grade solvents or better (St. Louis, MO, USA). Ethanol, 190 proof, and 5 N ammonium hydroxide were also purchased from Sigma-Aldrich. Clorox\textsuperscript{®} (Oakland, CA, USA) bleach was used to obtain the hypochlorite ion, present at an initial concentration of 6.15 % v/v. All adulterants were diluted in either deionized water, for optimization studies, or in a common beverage. The beverages which were used in these experiments included: Coca-Cola Classic\textsuperscript{®}, Mountain Dew\textsuperscript{®}, 2 % Milk, Ocean Spray\textsuperscript{®} Cranberry Juice, Tropicana\textsuperscript{®} Orange Juice, Dole\textsuperscript{®} Pineapple Juice, Pure Leaf\textsuperscript{®} Unsweetened Iced Tea, Red Bull\textsuperscript{®} Red Edition, Gatorade\textsuperscript{®} Fierce, Coors\textsuperscript{®} Light, Woodchuck\textsuperscript{®} Hard Cider, Sutter Home\textsuperscript{®} Pinot Noir, Absolut\textsuperscript{®} Vodka, Seven Tiki\textsuperscript{®} Spiced Rum, and 13th Colony\textsuperscript{®} Southern Corn Whiskey. Several dopants (hexanoic acid, linoleic acid, and methyl palmitate), purchased from AccuStandard (New Haven, CT, USA), were dissolved in hexane purchased from Fisher Scientific. Additionally a mass calibrant and independent quality assurance quality control (QA/QC) compound was run with each sample set to ensure a mass accuracy of $\pm 0.005$ Da. The mass calibrant used was polyethylene glycol 600 (PEG600) (Acros Organics, Geel, Belgium) dissolved in methanol. The independent QA/QC compounds used were reserpine and/or linoleic acid, dissolved in methanol. Tested samples were doped from 10 % volume fraction to 0.01 %
volume fraction. No greater concentrations were examined as the focus was on the adulteration of beverages, not analysis of neat adulterant.

Glass microcapillaries were used to introduce the samples into the DART gas stream. The 90 mm closed capillaries were purchased from Corning Incorporated (Corning, NY, USA). Before analysis, the capillaries were introduced into the gas stream for approximately 5 s to burn off any contaminants which may have been present on the rods. Samples were introduced to the DART gas stream for analysis by pipetting 1 µL aliquots of the sample, and dopant if applicable, onto the closed end of the glass capillary which was introduced into the DART gas stream.

Parameters for AccuTOF-DART

A JEOL (Toyko, Japan) AccuTOF™ mass spectrometer (JMS-T100LC) coupled with an IonSense (Saugus, MA, USA) DART® source was used. Both a DART-100 and DART-SVP source were used in these analysis. Ultra-pure helium was used as the ionizing gas and supplied at a flow rate of 1.75 L/min. For all analyses, the DART-100 source was set to a needle voltage of ±3,000 V while the DART-SVP was used with default voltages. Electrode 1 and electrode 2 voltages were set to ±200 V and ±225 V respectively. Mass spectrometer settings that were kept constant included an orifice 2 voltage of ±5 V and a ring lens voltage of ±3 V. Only DART-SVP data is shown since no significant differences were observed between the DART-100 and DART-SVP sources.

Two separate methods were developed for detection of these compounds, a positive ionization method for the detection of alcohols, acetone, ethylene glycol, and ammonia as well as a negative ionization method for the detection of the hypochlorite ion. Additional parameters for the positive mode method included an orifice 1 voltage of +10 V, a peaks voltage of 300 V, and a mass scan range of 30 m/z to 650 m/z at 0.5 seconds per scan. A helium gas stream temperature of 325 °C was also employed. For the negative mode, the gas stream temperature was set to 375 °C with an orifice 1 voltage of -10 V, a peaks voltage of 600 V, and a mass scan range of 65 m/z to 650 m/z at 0.5 s per scan.

Parameters for HS-GC/MS

In order to cross compare this technique to an existing analytical technique, analysis by headspace gas chromatography mass spectrometry (HS-GC/MS) was also completed. The instrument used was an Agilent 6890N gas chromatograph coupled to a 5975B inert XL mass spectrometer (Santa Clara, CA, USA) with a DB-1 column (30 m length × 250 µm i.d. × 0.25 µm film). Sampling of the adulterated aqueous solutions was completed by pulling 1 mL of the headspace from a sealed vial with an airtight syringe and then manually injecting the aliquot into the GC. GC parameters included an initial oven temperature of 40 °C with no ramp and a total run time of 6.0 min. A 30:1 split injection was completed, with an inlet temperature of 265 °C and a split flow of 29.0 mL/min. Helium was the carrier gas. A transfer line temperature of 285 °C was used with a mass scan range of 10 m/z to 120 m/z.

Limit of Detection Determinations

In order to determine the limit of detection for each of the adulterants by DART- MS, serial dilutions of the pure compounds were prepared in increments ranging from 1 % volume fraction to 0.001 % volume fraction in de-ionized water or the desired beverage. These dilutions were then run in triplicate by depositing 1 µL of both the dopant and sample onto a clean glass microcapillary and introducing it into the gas stream. The resulting mass spectra were then examined for the
presence of the adduct ion (with the exception of ethylene glycol, where the dimer ion was monitored) and searched against an in-house search library for mass accuracy. The limit of detection was defined as the lowest measured concentration at which the peak of interest was present at a signal-to-noise ratio of at least 3:1 in all replicates. Since this method was developed as a screening method, linear range was not examined.

**Results and Discussion**

*Method Optimization & Specificity*

Prior to analysis of adulterants in complex beverages, a number of different parameters were varied in order to determine the optimal conditions for the detection of these compounds. All nine of the compounds (acetone, methanol, ethanol, 1-propanol, isopropanol, 1-butanol, ethylene glycol, ammonia, and hypochlorite) were optimized individually as 0.1 % volume fraction solutions in de-ionized water, and those with like parameters were grouped together for further testing. Parameters that were optimized included ion polarity, gas temperature, orifice 1 voltage, and DART needle voltage. It was found that although alcohols responded in both positive and negative modes, the signal intensity was stronger (up to 10×) and low mass background was reduced using positive mode. Positive mode spectra of alcohols were found to produce predominantly protonated molecular ions and dimers, as well as dehydrated [m–OH]⁺ ions (Figure 1 and Figure S1). Similar results were observed for acetone and ethylene glycol (Figure 1 and Figure S2). In negative mode deprotonated molecular ion and dimers dominated the spectra (Figure S3). With the exception of acetone, the dimer ion was identified as the strongest signal in all organic samples. Hypochlorite was only detected in negative mode and ammonia was only detected in positive mode, as expected, since both are pre-formed ions (Figure S4). These compounds were difficult to detect without the use of a dopant species. Table 1 highlights characteristic peaks seen for all adulterants.

The parameter that provided the greatest variation in signal intensity was DART gas stream temperature. The temperature of the gas affects the rate of desorption of the sample off of the surface, with increased desorption occurring at increased temperatures. In most instances, there is also an upper limit to the optimal temperature due to thermal degradation or flash desorption of the sample. Gas stream temperature was incrementally increased from 150 °C to 400 °C. For the organic species, optimal response was found in the range of 300 °C to 400 °C, with some compounds exhibiting a marked decrease in signal above 350 °C (Figure 2). Ammonia, which is also volatile, responded best at approximately 400 °C. Hypochlorite, which has a substantially lower vapor pressure, also required the higher gas stream temperature for effective desorption to occur.

Another instrumental parameter that was investigated was the degree of in-source collision induced dissociation (CID) (adjusted using the orifice 1 voltage). The voltage difference between the first and second orifice plates controls the extent of fragmentation due to increased collisions with accelerated ions in the differentially pumped region of the mass spectrometer. As shown in Figure 3, a low orifice voltage of +10 V produced a strong signal for the organic compounds. At this low orifice voltage, dimerization and trimerization were observed for the organic species. The low orifice voltage also aided in adduct formation with the dopant species (Figure 3C). As the orifice voltage was increased, increased collisions caused a noticeable reduction in dimer and trimer formation, as well as an increase in the base peak of the compound (Figure 3B). This may allow for an enhancement in sensitivity and simplicity of the spectra when neat compounds are analyzed. However, when a dopant species was introduced at the higher orifice voltage (Figure
3D), sufficient collisions existed to inhibit nearly all adduct formation and effectively eliminate the benefit of dopant introduction. When higher orifice voltages were used (60 V to 90 V), the compounds of interest were completely fragmented and could no longer be distinguished from background. The inorganic compounds, which existed as pre-formed ions, benefited from a slightly higher orifice 1 voltage, as they readily formed large clusters at low voltages. However, because it was determined that sensitivity could be increased with adduct formation, a low orifice 1 voltage of ±10 V was used for all analyses. The DART needle voltage, which was varied from ±2,500 V to ±4,500 V was found to have a negligible effect on all compounds tested.

**Dopant Introduction**

Once optimal methods were established for measuring adulterant chemicals, studies were completed to determine whether the sensitivity and specificity of the technique could be enhanced. While the signal of the organic compounds was strong when analyzed in an aqueous solution, the complexity of beverages caused significant background in the low mass region (below 150 m/z), as well as competitive ionization with the compounds of interest. These issues further complicated the analysis of ammonia and hypochlorite, whose signals were low even when analyzed as aqueous mixtures. To enhance detection of these compounds in complex mixtures, the addition of a dopant to the sample was investigated.

Several criteria were used to establish possible dopants to investigate including: ease of accessibility, cost, solubility in a solvent not already being screened for (e.g., hexane), and easily ionized by DART. Additionally, the dopants chosen would not be compounds traditionally found in beverages and would not interfere with other potential forensic investigations or food safety screening (i.e. the use of a narcotic as a dopant). Based on these criteria, a number of dopants were chosen for analysis and included fatty acids, fatty acid methyl esters, and glycol ethers. These compound classes were chosen because they have been found to adduct readily with a number of species (such as nitrate or water). Also, they had polarities which were similar to the compounds of interest. A range of sizes within each class were also examined to evaluate if relative volatility to the adulterants played a role in adduct formation. Because adduct formation is desired, a high concentration of the dopant was added to the sample to ensure an excess of adduct molecules.

Dopants were introduced to the sample by pipetting 1 µL of the diluted dopant (at a concentration of approximately 5 mg/mL in hexane) onto the glass sampling rod, allowing the hexane to evaporate, and then pipetting 1 µL of the sample onto the rod. This method minimized contamination of the dopant. Excess dopant was used in all cases to maximize adduct-adulterant interactions. It was also found that deposition order was necessary for enhanced detection where deposition of the solution prior to the dopant lowered the adduct response, potentially due to the need for the dopant molecule to be desorbed first or a hydrophobic / hydrophilic interaction between hexane and the beverage which separated the species. In total, twelve dopant species were examined and included: hexanoic acid, heptanoic acid, hexadecanoic acid, octadecanoic acid, oleic acid, linoleic acid, methyl hexanoate, methyl decanoate, methyl palmitate, 2-ethoxyethanol, 2-butoxyethanol, and di(ethylene glycol) ethyl ether. These compounds were chosen as representative chemicals spanning a range of the three classes of interest. Efficacy of these compounds as potential dopants was evaluated by analyzing each of the nine adulterants, as 0.1 % v/v aqueous solutions, individually and in the presence of each of the twelve dopant species in their respective ionization modes. Peak areas of the adduct species, if formed, were integrated and used to cross compare the efficacy of the dopants for organic compounds, ammonium hydroxide, and sodium hypochlorite.
For the organic adulterants it was found that short chain fatty acids such as hexanoic acid and heptanoic acid provided the best response. Typical adducts formed with the short chain fatty acids were [M+adduct–OH]+ ions for the straight chain alcohols and [M+adduct+ H]+ ions for 2-propanol (branched alcohol) and acetone. It is currently unclear why the adduct ion formed was dependent on whether the molecule was straight or branched, though it may offer a method to differentiate between 1-propanol and 2-propanol isomers. Table 2 shows the molecular formula and exact masses for the various adducts which were formed. Large chain fatty acids, such as hexadecanoic acid and octadecanoic acid, only slightly formed adducts with the larger alcohols like 1-butanol, or with acetone. The lack of adduct formation may be due to differences in volatility between the sample and dopant or more likely is the result of steric hindrances making adduct formation difficult. Detection of ethylene glycol was not improved by dopant addition. Though adduct molecules were created using many of the dopants, the most intense peak was consistently the molecular dimer. The unsaturated fatty acid methyl esters and fatty acids produced a low response to the organic compounds. Glycol ethers also produced a poor response, likely because they would dimerize and trimerize with themselves.

Optimal adduct formation with ammonia was observed with long chain fatty acid methyl esters, which formed [M+NH4]+ ions. Enhanced detection with long chain fatty acid methyl esters may have occurred because of increased proton affinity of the methyl esters in comparison to the shorter chain compounds. Of the different methyl esters, methyl pentadeconate was chosen as the optimal dopant species for ammonia detection. Adduct formation with fatty acid molecules was possible, forming [M+NH4]+ ions, but a significantly lower response was observed than with the fatty acid methyl esters. Similar to the organic adulterants, glycol ethers provided little improvement to ammonia detection.

Adduct formation with the hypochlorite ion was found to be more problematic than the other compounds, likely due to decreased volatility making thermal desorption difficult. Only unsaturated fatty acids were found to produce adduct ions with hypochlorite, forming both [M+ClO]– and [M+Cl]– ions. Because a chloride adducted species was formed it was thought that this dopant may not be specific to hypochlorite and could also be formed by the presence of other chloride containing salts. To determine if hypochlorite could be misinterpreted by other chloride containing species, 1 % volume fraction aqueous solutions of sodium chloride, potassium chlorate, and ammonium perchlorate were analyzed with the incorporation of linoleic acid to identify potential adducts that were formed. The adducts at 315 m/z, 317 m/z, 331 m/z, and 333 m/z were found to be specific to hypochlorite (Figure S4).

Analysis of Complex Mixtures

In order to establish the feasibility of this method for real-world samples, fifteen beverages were spiked with each of the nine adulterants, at 0.1 % volume fraction, with the exception of ethanol which was not analyzed in alcoholic beverages. The beverages chosen included six alcoholic beverages, three juices, two sodas, milk, iced tea, a sports drink, and an energy drink. Beverages were adulterated, in addition to aqueous solutions, to investigate whether or not the presence of sugar, sweeteners, salts, preservatives, flavors, and other compounds would complicate detection and/or specificity of the technique. Alcoholic beverages were also chosen to evaluate whether or not the adulterants could be detected in solutions containing a high concentration of ethanol. To evaluate feasibility the 0.1 % volume fraction adulterated solutions were analyzed, in triplicate, using the appropriate dopant. Controls of each beverage without an adulterant, both with and without the dopants, were also analyzed to determine if any false
positives would be present. Determination of peak presence was completed by searching against an in-house search list developed from the peak identities of both the adducted and unadducted aqueous solutions. The search parameters used required a peak to be greater than 1 % relative intensity and within ±0.005 Da of the theoretical mass to be identified.

Figure 4 highlights representative mass spectra of pineapple juice and pinot noir, each adulterated by 1-butanol. Detection of adduct peaks in non-alcoholic adulterated beverages was largely successful (Table S1) with all adulterants detectable at a level of at least 1 % volume fraction. With the exception of the energy drink and milk, detection of adulterants was possible at levels below 0.1 % volume fraction. No peaks were found in the controls that overlapped with the ions of interest that would have caused false positives. In several instances, control spectra did produce peaks at the same nominal mass as ions of interest but they did not fall within the ±5 mmu mass tolerance used in the peak search. In many of the spectra the molecular ion of the adulterant was also present, in addition to the adduct ion, indicating detection could be completed at levels well below the 0.1 % volume fraction level.

Detection of adulterants in alcoholic beverages proved to be more difficult than in non-alcoholic beverages (Figure 4 and Table S1). Since the concentration of ethanol in all cases was much higher than that of the adulterant, the dopant preferentially formed adducts with the available ethanol molecules. This competition resulted in the inability to detect both methanol and 2-propanol in any of the alcoholic beverages. Levels of methanol and 1-propanol were increased to 1 % volume fraction, and detection was still not possible. Detection of 1-butanol, and acetone, however, was possible at the 0.1 % volume fraction level while detection of 1-propanol appeared to be dependent on ethanol concentration. Because of the abundance of ethanol molecules, the adulterant ion signal was suppressed to near the 1 % relative intensity threshold used for the search, and well below the response in non-alcoholic beverages. However, the incorporation of the dopant species enhanced sensitivity by providing a second peak to monitor that was not overlapped, as shown in for 1-butanol in white wine (Figure 4E and 4F). Detection of ethylene glycol, ammonia, and hypochlorite were not affected likely because no dopant, or a different dopant, was required for these compounds. Additional work is looking to identify methods for the detection of methanol and 2-propanol from alcoholic beverages by using different dopants or altering instrumental parameters.

Limits of Detection

The limit of detection for adulterants diluted in both deionized water and several beverages was determined for DART-MS. Adduct formation was used, with the exception of ethylene glycol (in which the dimer was monitored), for limits of detection determination and analysis of complex mixtures. Table 3 highlights the limits of detection, which ranged from 0.001 % volume fraction to 0.1 % volume fraction, for all species analyzed. Limits of detection were found to be lowest for the least complex beverages, i.e., water and iced tea, while more complex beverages required more adulterant to be present for accurate detection. For alcoholic beverages, the limits of detection were amongst the highest, because the presence of ethanol in the beverage which caused competitive and preferential adduct formation. As the alcohol content was increased, the limit of detection for the adulterants also increased. These limits of detections were compared to those identified by headspace gas chromatography mass spectrometry (HS-GC/MS) for applicable compounds (all compounds except ammonia and hypochlorite). HS-GC/MS was chosen because this is the technique commonly employed by forensic laboratories for this type of analysis. Only aqueous solutions were analyzed using HS-GC/MS, and DART-MS was found to have sensitivity
that was equal to or greater than those obtained by HS-GC/MS (Table 3). Coupled with rapid analysis time and a wider range of chemicals detectable, this increased sensitivity further highlights the use of DART-MS as a viable screening tool for adulterants in beverages.

**Conclusions**

Rapid, sensitive, and specific detection of adulterants has been demonstrated using DART-MS. Introduction of a dopant allowed for adduct formation, which was shown to enhance the sensitivity and specificity of the investigated adulterants, for both organic and inorganic compounds. Fifteen beverages were adulterated, and detection of all nine adulterants was possible, with the exception of methanol, 1-propanol, and 2-propanol in alcoholic beverages. These compounds were detectable in the range of 0.001 % volume fraction - 0.1 % volume fraction, which was as sensitive or more sensitive than HS-GC/MS for detection of the same organic adulterants. This technique also provides a method for the detection of inorganic components such as ammonia and hypochlorite, which HS-GC/MS cannot detect. Differentiation of isomeric compounds, namely 1-propanol and 2-propanol, was also observed and attributed to different pathways for adduct formation but requires further work in validation. Future work will focus on expanding the adulterants that can be screened for, as well as establishing methods that would allow for the successful detection of adulterants like methanol in an ethanol-containing beverage. Quantification of the nine adulterants using DART-MS is also being explored.

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References

Table 1. Peaks obtained when adulterants are analyzed as 0.1 % v/v aqueous solutions in positive ionization mode. “M” refers to an intact molecule of the specific compound. The mass containing an asterisk (*) was the base peak observed in the spectra.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Dopant</th>
<th>m/z</th>
<th>Molecular Formula of Adduct</th>
<th>Adduct Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>HA</td>
<td>131.1072</td>
<td>C₇H₁₅O₂</td>
<td>[HA+Methanol-OH]^+</td>
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<td>Ethanol</td>
<td>HA</td>
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<tr>
<td>2-Propanol</td>
<td>HA</td>
<td>177.1491</td>
<td>C₉H₁₉O₂</td>
<td>[HA+Propanol+H]^+</td>
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<td>Butanol</td>
<td>HA</td>
<td>173.1541</td>
<td>C₁₀H₂₁O₂</td>
<td>[HA+Butanol-OH]^+</td>
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<td>Acetone</td>
<td>HA</td>
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<tr>
<td>Ammonia</td>
<td>MP</td>
<td>288.2902</td>
<td>C₁₆H₃₆O₂N₁</td>
<td>[MP+NH₄]^+</td>
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<td>Hypochlorite</td>
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<td>C₁₈H₃₂O₂Cl₁</td>
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<td></td>
<td>LA</td>
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<tr>
<td>Ethylene Glycol</td>
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<td>161.1178</td>
<td>C₈H₁₇O₃</td>
<td>[HA+Ethylene-OH]^+</td>
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</table>

Table 2. Adulterants and the dopants which were used to form adduct ions. The molecular formula was derived from the accurate mass of the adduct ion, which allowed for an assignment of each to be made. Under the dopant and adduct assignment columns “HA” represents hexanoic acid, “MP” represents methyl palmitate, and “LA” represents linoleic acid. *For ethylene glycol, though the presence of a dopant did not enhance detection of the compound, it was found to adduct with hexanoic acid.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Aqueous Solution (% v/v)</th>
<th>Pineapple Juice (% v/v)</th>
<th>Soda (% v/v)</th>
<th>Wine (% v/v)</th>
<th>HS-GC-MS (% v/v)</th>
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</thead>
<tbody>
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<td>Methanol</td>
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<td>0.025 %</td>
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<td>0.5 %</td>
</tr>
<tr>
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<td>0.01 %</td>
<td>0.025 %</td>
<td>N/A*</td>
<td>0.5 %</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>0.01 %</td>
<td>0.01 %</td>
<td>0.01 %</td>
<td>ND</td>
<td>0.5 %</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>0.01 %</td>
<td>0.05 %</td>
<td>0.025 %</td>
<td>0.1 %</td>
<td>0.5 %</td>
</tr>
<tr>
<td>Butanol</td>
<td>0.01 %</td>
<td>0.01 %</td>
<td>0.025 %</td>
<td>0.1 %</td>
<td>0.5 %</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.001 %</td>
<td>0.005 %</td>
<td>0.0025 %</td>
<td>0.01 %</td>
<td>0.5 %</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.001 %</td>
<td>0.025 %</td>
<td>0.05 %</td>
<td>0.05 %</td>
<td>N/A**</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>0.001 %</td>
<td>0.025 %</td>
<td>0.05 %</td>
<td>0.05 %</td>
<td>N/A**</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>0.01 %</td>
<td>0.01 %</td>
<td>0.01 %</td>
<td>0.05 %</td>
<td>0.01 %</td>
</tr>
</tbody>
</table>

Table 3. Limits of detection determined for the nine adulterants in aqueous solutions and select beverages, when analyzed by DART-MS, and in aqueous solutions when analyzed by HS-GC-MS. The limits of detection are expressed as percent by volume when diluted in the beverage. A single asterisk (*) indicates the adulterants was not detectable because the beverage contained that compound. Double asterisk (**) indicates that the adulterant was not capable of being analyzed by HS-GC-MS and thus no limit of detection is available. An “ND” indicates that the compound was not detectable at a level equal to or lower than 1 % v/v.
Figures:

Figure 1. Positive ion mass spectra of 0.01 % v/v aqueous solution containing ethanol (A.) and the same solution in the presence of the dopant, hexanoic acid (B.). Positive ion mass spectra of 0.01 % v/v aqueous solution containing ethylene glycol (C.) and the same solutions in the presence of hexanoic acid (D.). Select peaks relating the compound of interest (red), the dopant (blue), and the adduct formed with the dopant (yellow) are also shown.

Figure 2. Response of select analytes across a range of DART gas stream temperatures as a function of maximum signal intensity. Abbreviations for the analytes are methanol (MeOH), 1-propanol (PrOH), acetone (Ace), and ethylene glycol (EG).
Figure 3. Positive ion mass spectra of 1-butanol as a 0.1 % v/v aqueous solution both without (A. & B.) and with the presence of hexanoic acid (C. & D.) at a low, 10 V, orifice 1 voltage (A. & C.) and higher, 30 V, orifice 1 voltage (B. & D.). The analyte peak highlight is the [M-OH]+ ion of 1-butanol (57 m/z).

Figure 4. Positive ion mass spectra of pineapple juice (A.) and white wine (C.) with the hexanoic acid dopant as well as pineapple juice (B.) and wine (D.) spiked to 0.1 % v/v 1-butanol with hexanoic acid. To highlight the presence of the butanol adduct and lack as specificity using the
base peak for 1-butanol, overlaid enlarged mass spectra of the [M-OH]$^+$ ion of 1-butanol (E.) and the 1-butanol hexanoic acid adduct (F.) are also shown.