C.) TID-1 Detection of Vanillin in Wine and Flavored Tea Samples. It was known from prior work with TID-1 detection on an Agilent 6890 GC that this mode of detection provides an especially large response to Vanillin in comparison to many other oxygenated compounds. Figure 4 shows TID-1 chromatograms for a diluted sample of imitation Vanilla flavoring and a sample of Vanilla flavored tea (Bigelow Vanilla Chai blend). Figure 5 shows the detection of Vanillin in a sample of Merlot Wine. These data provide a good illustration of the applicability of the compact SRI/DET analyzer to the selective detection of oxygenated flavor and aroma constituents of real world samples.

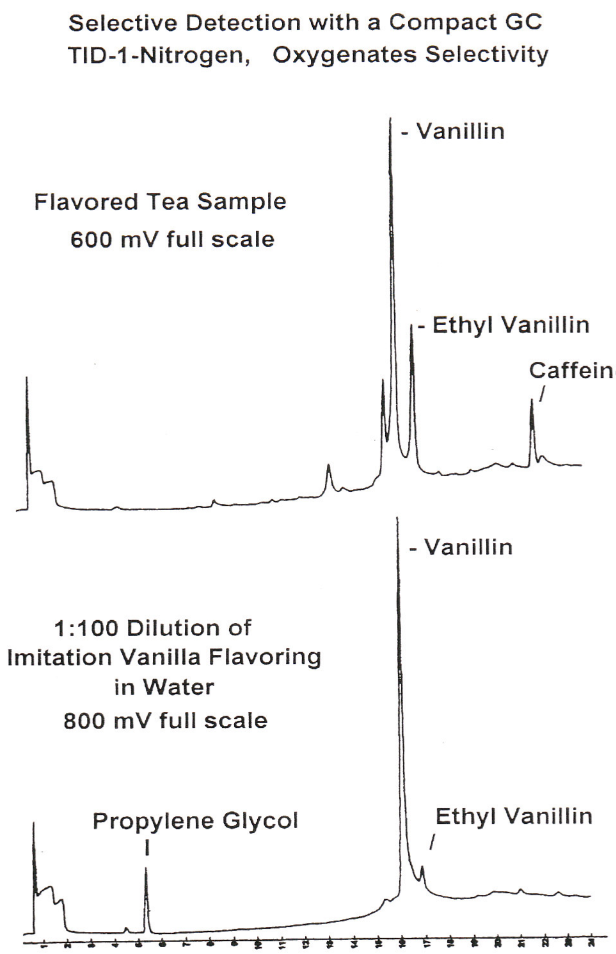

Figure 4. Direct injections of 1.3μL of each sample. Top chromatogram, Bigelow brand Vanilla Chai tea. Bottom chromatogram, 1 to 100 dilution in Water of an Imitation Vanilla Flavoring product. Same column as Figure 1. He carrier programmed 10 - 25psi @ 0.75psi/min, 25psi - 4min. Column temperature programmed 60 - 260°C @ 10°C/min, 260°C - 4min. Injector=260°C, detector=275°C. TID-1 conditions same as Fig. 1.

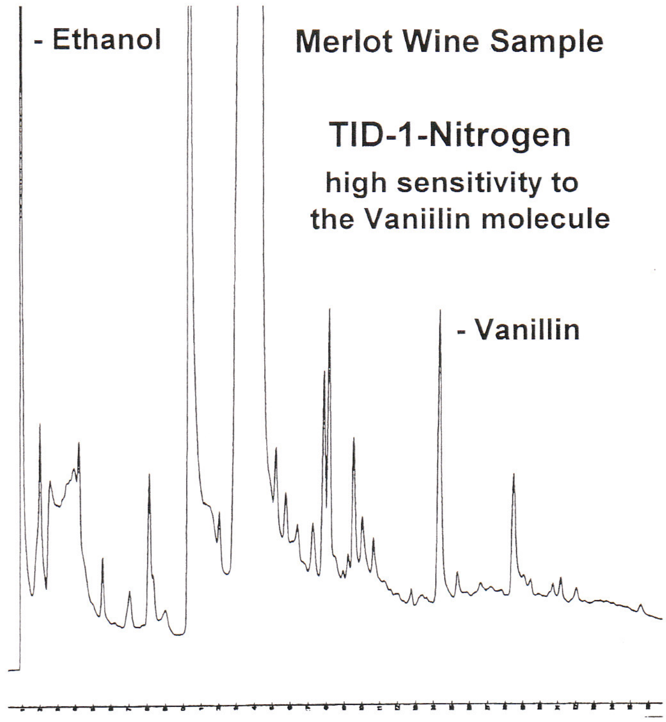

Figure 5. Direct injection, 1.5μL Ravenswood Merlot wine. Same column as Figure 1. He carrier programmed, 10-25psi @ 0.45psi/min, 25psi - 4min. Column temperature programmed, 60-260°C @ 6°C/min, 260°C - 4min. Injector and detector same as Figuire 4. TID-1 conditions same as Figure 1.

D.) TID-1 Detection of Glycerol in Wine Samples. Data in Figures 1 - 5 were obtained using a 15 m x 0.32 mm fused silica column coiled onto a 3 inch diameter x 1 inch high cage from Quadrex. We have also had success recoiling other 0.32 mm fused silica columns into 3 - 3.5 inch diameter bundles held together by soft Aluminum straps. Data in this and the following section were generated with such a 20 m x 0.32 mm bundled column with a 0.25 μm AT-Aquawax coating from Alltech Associates.

Like Vanillin, Glycerol is another oxygenated compound which has a very large response in the TID-1 mode of detection. This is demonstrated in Figure 6 which shows the Gylcerol signal in a wine sample (Shiraz varietal) in comparison to the TID-1 signals from Ethanol and Acetic Acid. As in the earlier samples, this was a direct injection of the wine into the glass lined flash vaporization injector of the SRI/DET analyzer. Like the earlier tea samples, non-volatiles in the wine were left as deposits inside the glass liner of the injector.

DET REPORT

NO. 52 SEPTEMBER 2006

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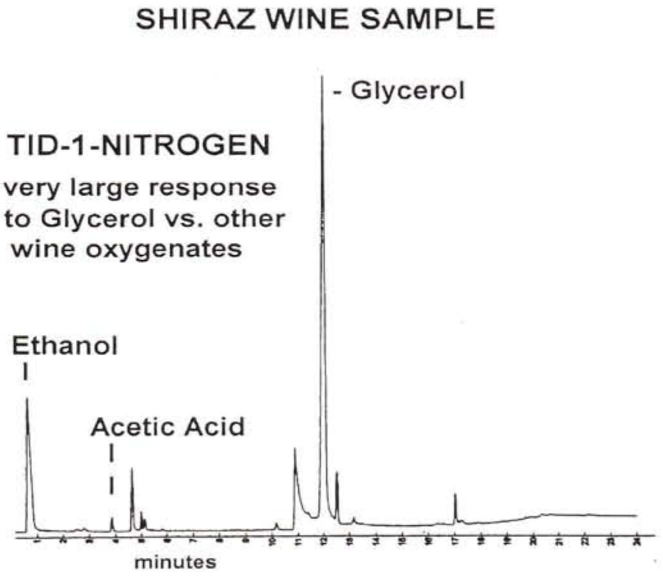

Figure 6. Direct injection of 0.5µL Shiraz Wine sample. 20m x 0.32mm x 0.25µm AT-Aquawax (Alltech) bundled into 3 - 3.5 inch coil. He carrier programmed, 18 - 33psi @ 0.75psi/min, 33psi - 4 min. Column temperature programmed 60 - 260°C @ 10°C/min, 260°C - 4 min. Injector & detector = 260°C. TID-1 conditions same as Figure 1.

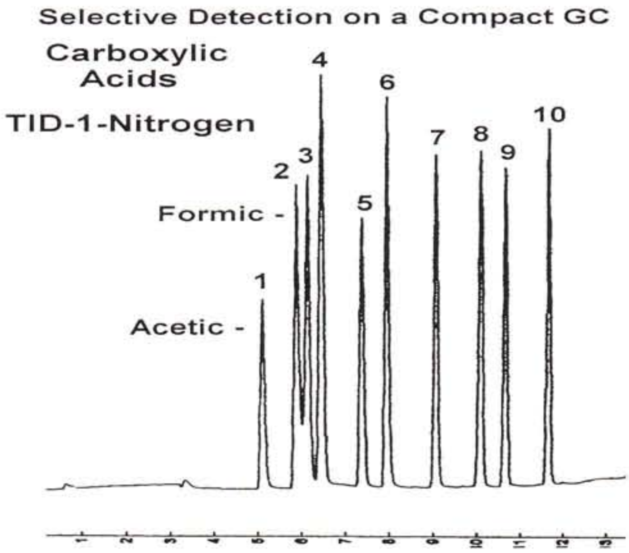

Figure 7. Direct injection, 1.0µL Supelco Acid mix, 10mM each in Water solution, 1-Acetic, 2-Formic, 3-Propionic, 4-iso-Butyric, 5-Butyric, 6-iso-Valeric, 7-n-Valeric, 8-iso-Caproic, 9-n-Caproic, 10-Heptanoic. Same column as Figure 6. He carrier, 18-22.5psi @ 0.45 psi/min. Column temperature, 60-120°C @ 6°C/min.

E.) TID-1 Detection of Acetic, Formic, and Other Volatile Acids. Volatile Carboxylic Acids are another class of oxygenates that generate especially large responses in the TID-1 mode of thermionic detection. Figure 7 shows a TID-1 analysis of a mix of volatile acids in water (Supelco mix 46975-U). Unlike an FID, TID-1 responded to Formic Acid as well as all the other acids in the mixture. Also unlike an FID, Nitrogen sufficed as the only detector gas required (i.e., no Hydrogen needed).

Figure 8 shows TID-1-Air detection of Acetic and Formic Acids in a wine sample. In this analysis, Air was used as the detector gas in order to suppress the response to Ethanol and some other wine oxygenates relative to the Volatile Acids. In analyses of alcoholic beverages, a tell tale difference between TID-1-Nitrogen and TID-1-Air chromatograms is an increased response to the Water content of the sample when Air is the detector gas. Among the thousands of reports of wine analyses, very few mention the detection of Formic Acid. We believe that is because an FID is simply not sensitive to this compound, and most previous wine analyses have used FID detection. Consequently, one of the interesting applications of TID-1 detection is the examination of wines and other alcoholic beverages for the presence of Formic Acid, as well as its relative magnitude versus Acetic and other volatile acids.

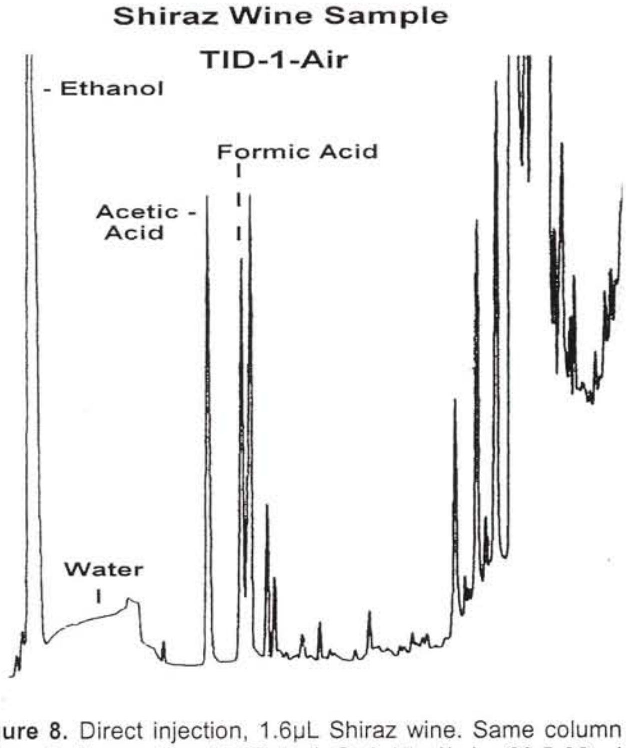

Figure 8. Direct injection, 1.6µL Shiraz wine. Same column as Figure 6. He carrier, 18-22.5psi @ 0.45psi/min, 22.5-33psi @ 1.50psi/min, 33psi - 4min. Column temperature, 60-120°C @ 6°C/min, 120 -260°C @ 20°C/min, 260°C - 4min.

2.) EASY CONVERSION OF AGILENT 6890 NPD EQUIPMENT TO OXYGENATE SELECTIVE DETECTION.

The NPD hardware on the Agilent 6890 GC was designed to accommodate the ion source structures developed by DET. These are cylindrically shaped, ceramic coated elements of approximately 1/16 inch diameter, extending out from a hexagonally shaped Stainless Steel mounting flange. These same ion source structures are also used in the compact SRI/DET analyzer described in the previous section of this report.

Development of ceramic coating formulations for surface ionization applications constitutes DET's main business. There are 2 formulations that have been optimized for use in NPD's like that of the 6890 GC. One is a Black Ceramic formulation (TID-2 type) that was specifically designed to produce sharp peaks for P compounds. Tailing of P peaks had previously been a notorious characteristic of NPDs. The Black Ceramic formulation is recommended for applications requiring P or both P and N detection (e.g., pesticides). A second White Ceramic formulation (TID-4 type) was developed to provide the best possible N response without concern for optimum P-tailing characteristics. This White Ceramic formulation is recommended for applications requiring only N detection (e.g., drugs of abuse).

In addition to ion sources for NP detection, DET has developed several other ceramic coating formulations for other modes of selective detection. One of these is a TID-1 type coating discussed in the preceding section for use in selective detection of Oxygenates. A TID-1 ion source has exactly the same dimensions as the NP ion sources, so it fits easily into the Agilent 6890 NPD hardware structure.

TID-1 detection uses a simpler detector gas environment than an NPD. On the 6890 GC, conversion from NPD to Oxygenate selective detection involves turning OFF the NPD Hydrogen flow, and connecting either Nitrogen or Air gas supplies to the detector "Makeup" and "Air" lines. The selection of Nitrogen or Air or some mixture of each depends on what type of Oxygenates are being detected. For example, best selectivity and sensitivity for most Oxygenates is obtained with Nitrogen. With Air, TID-1 response to Oxygenates like Alcohols, Aldehydes, and Ketones is reduced substantially while Phenols, Carboxylic Acids, and Glycol responses remain large. Water Vapor is also best detected with an Air detector gas environment.

Optimum TID-1 detection also requires a larger polarization voltage than is available from the 6890 NPD Bead Voltage supply. This can be provided by replacing the 6890 Bead Voltage by a stand-alone DET Current Supply module. The DET module has dimensions of 5 ½ inches high x 6 inches wide x 10 ½ inches deep, and it fits conveniently on top or alongside the 6890 instrument. It features a four digit Thumbwheel setting of heating current for the ion source, and switch selection of 3 polarization voltages for optimum operation of TID-1, NPD, and other modes of thermionic detection. This is exactly the same DET module used in the SRI/DET equipment discussed in the preceding section of this report.

The DET Current Supply provides a Constant Current type of power for heating the ion source in contrast to the 6890 Bead Voltage supply which provides a Constant Voltage type heating. The surface temperature of the ion source is determined by the magnitude of electrical current flowing through the source's resistive core, and Constant Current power maintains that at a controlled constant value. With Constant Voltage power, the magnitude of heating current through the source's core is susceptible to thermal equilibration changes in the resistance of the source's core as well as in the lead wires leading to the ion source. Hence, an added advantage of the DET Current Supply module is that it provides the most stable means of powering the ion sources used in TID-1, NPD, and other modes of thermionic detection.

Another advantage of Constant Current powering of the ion source is that a long cable can be used to connect the ion source to the power supply. A 4 foot long cable is provided with the DET Current Supply. With this cable, replacement of ion sources is greatly facilitated because the 6890 GC instrument side panels do not have to be removed to gain access to the connector on the source cable.

Still another feature of the DET Current Supply is that it has a Green/Red front panel status light to provide an immediate indication in the event there is an open circuit in the source wiring due to burn out of the source's wire core. With the 6890 NPD's Bead Voltage supply, the detector readout will indicate an increasing bead voltage value even when there is no ion source at all connected to the power supply.

Conversion of the 6890 NPD equipment to Oxygenate

selective detection, therefore, involves three simple and inexpensive changes as follows:
1.) installation of a TID-1 ion source ($285) in place of the NP ion source; 2.) supplying N_2 or Air as the only detector gas required; and 3.) substituting a DET Current Supply module ($1760) for the 6890 NPD Bead Voltage supply as the means of powering the ion source. The 6890 NPD Electrometer works just fine for TID-1, NPD, or any other mode of thermionic ionization detection, so the detector output to a data system is the same as standard NPD operation.

Figure 9 compares TID-1-Nitrogen selective detection versus FID detection for a complex Hydrocarbon sample matrix. For the gasoline sample shown, the analysis of Ethanol required only Nitrogen for both the GC carrier and detector gases, and short analysis times were possible because Ethanol was easily detected amongst the many co-eluting Hydrocarbons.

Figure 10 compares TID-1-Oxygen selective detection versus FID detection for an complex Oxygenate sample matrix. In this case, Oxygen was used as the detector gas in order to suppress TID-1 responses to Ethanol and some other Oxygenates while still maintaining a good response to the BHA and BHT Phenolic Antioxidants in the Essential Oil sample.

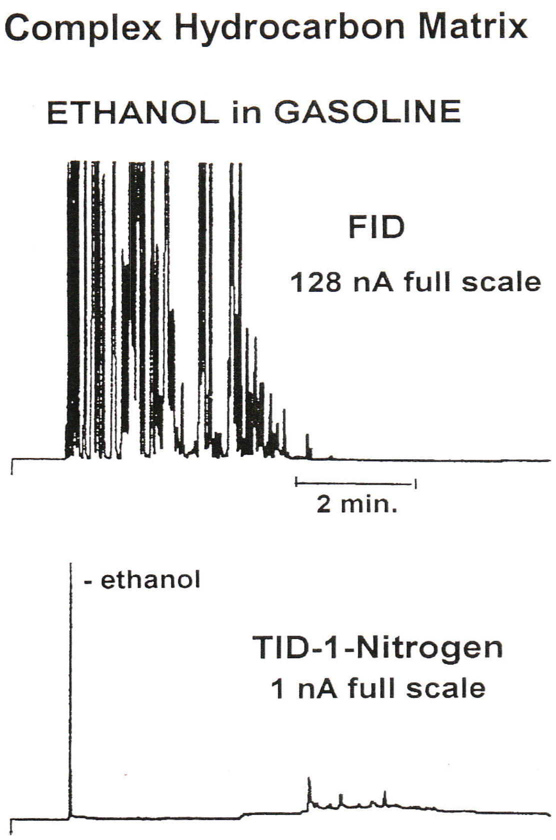

Figure 9. Inject 0.2µL gasoline. 30m x 0.53mm HP-1, N_2 carrier = 8mL/min, 40°C - 1.5min, 40 - 240°C at 40°C/min, 240°C - 3min. TID-1 ion source mounted in 6890 NPD hardware and powered with a stand-alone DET Current Supply. Detector gases: N_2=10 and 50ml/min through makeup and "air" lines, respectively. TID-1 source heat=2.35 A, polarization = - 45V.

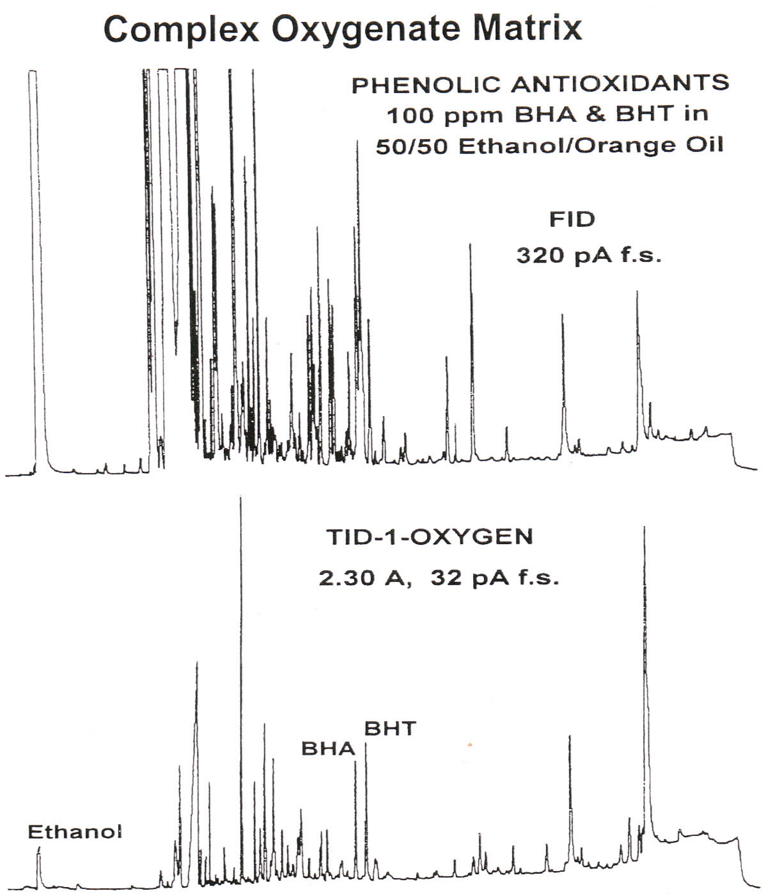

Figure 10. Inject 0.7µL 50/50 mix of Ethanol/Orange Oil sample with 100ppm BHA & BHT. 30m x 0.53mm DB5ms, He carrier = 6mL/min, 70°C - 2min, 70-150°C at 20°C/min, 150-260°C at 7°C/min, 260°C - 1 min. Detector gases: O_2 = 10 and 50mL/min. TID-1 source in 6890 NPD hardware and powered with DET Current Supply. TID-1 source heat = 2.30 A, polarization = - 45 V.