

DET

innovations in chemical detection

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ECHnology Pty Ltd
Australian Distributors; Importers & Manufacturers

COMPACT GC ANALYZER for selective detection of **OXYGENATES & NITRO COMPOUNDS** OR **NITROGEN-PHOSPHORUS COMPOUNDS** **(NPD)**



GC SPECIFICS

- SRI Instruments model 310 is an easily portable small size & weight.
- heated flash vaporization injector with a deactivated glass liner.
- accommodates one 15m or 30 m x 0.53mm metal capillary column.
- heated detector base.
- electronic pressure control of carrier & 2 detector gases.
- built-in data system provides signal measurement plus capability for programmed column temperature & carrier gas pressure when coupled to a laptop computer.

SELECTIVE DETECTION SPECIFICS

- DET Thermionic Ionization Detector hardware features concentric cylinder geometry for streamlined gas flow and most efficient ion collection.
- ceramic coated Thermionic Ion Sources are mounted on a self-aligning flange for easy interchangeability.
- TID-1 type ion source provides selectivity for Oxygenates and Nitro-compounds with just Nitrogen or Air as the detector gas; also non-destructive so sample aromas can be sensed at the detector exit.
- Nitrogen-Phosphorus selectivity (NPD) provided by TID-2 type ion source for sharpest P peaks, or by TID-4 ion source for best possible N response.
- stand-alone DET Current Supply provides precision thumbwheel control of ion source heating power plus switch selection of different polarizations for optimum response in all modes of detection.

NEW PRODUCT ANNOUNCEMENT JUNE 2006

COMPACT GC ANALYZER FOR SELECTIVE DETECTION OF OXYGENATES OR NITROGEN-PHOSPHORUS COMPOUNDS

DETECTOR Engineering & Technology has combined its Thermionic Ionization Detector equipment with an SRI Instruments Model 310 GC to provide a compact GC analyzer for the selective detection of either Oxygenates and Nitro-compounds, or for the selective detection of Nitrogen-Phosphorus compounds (i.e., NPD). Selectivity is determined by the type of ceramic coated Thermionic Ion Source installed in the detector, and the composition of detector gases supplied. One type of selective detection can be easily and inexpensively adapted to the other type by changing the ion source and reconfiguring the detector gases. A stand-alone DET electronics module provides precision controlled power for the Ion Source, while SRI's NPD type amplifier provides signal measurement. SRI's built-in PeakSimple™ software in the GC allows operational control and signal processing to be accomplished by connection to a laptop computer. The equipment is small in physical size and weight, and is easily transported on the seat of a small sedan.

GC Specifics. Dimensions of the SRI 310 GC are 12.75 inches wide, 14.75 inches deep, 12.75 inches tall, and the weight is 32.5 pounds. The column oven accommodates 15m or 30m long, 0.53mm diameter metal capillary columns (MXT® type from Restek, or Ultra-ALLOY™ type from Quadrex) formed in 3.0 inch diameter coils. The GC is equipped with a heated Flash Vaporization Injector: a heated detector base; and electronic pressure control of the column carrier gas and two detector gases. The detector gas lines are configured with restriction tubing normally used for supplying Hydrogen and Air to the SRI NPD, and signals are measured with the SRI NPD amplifier. In the case of Oxygenates detection, either Nitrogen or Air are supplied through the two detector gas lines. SRI's built-in PeakSimple™ data system provides data acquisition, as well as capability for programmed control of both column temperature and carrier gas pressure.

DET Modifications to the SRI GC. A Twinex chassis connector is mounted on the right side external wall of the GC, and a cable is routed internally to the detector vicinity to allow control of ion source power with a stand-alone DET module. The Flash Injector is modified by insertion of a 72

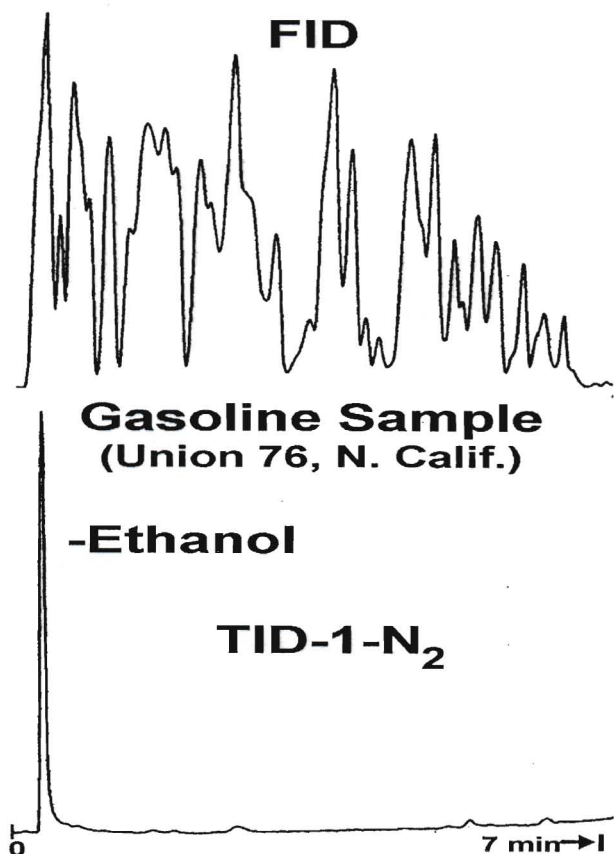
cm long direct injection glass liner (Restek part # 20345). A 4 inch length of uncoated, deactivated 0.53mm fused silica tubing is press-tight sealed into the injector liner, and extends into the column oven where it connects to the metal capillary column with a low volume stainless steel adaptor fitting which has been deactivated by Restek's Siltek® process. SRI's original 1/8 inch to 0.8mm Graphite seals for the injector and detector ends of the column have also been replaced by 1/8 inch tube to 1/16 inch Swagelok® reducer fittings and smaller diameter 1/16 inch x 0.8 mm Graphite ferrule seals. The smaller Graphite ferrules provide a more reliable seal and are less likely to stick in the fitting upon removal.

DET Detector Hardware. The Thermionic Ionization hardware includes a ceramic tipped jet structure that guides the end of the metal capillary column into the heated detector base. The detector structure provides a preferred ionization geometry with the cylindrically shaped ion source located on the axis of a collector electrode cylinder. This configuration provides a streamlined flow of gases through the detection volume, and an optimum electric field for collection of ions. Ion sources used in this equipment attach to the detector structure with 3 screws, and are self-aligning without any additional positioning. These ion sources are identical in structure, and are interchangeable with those used in the Agilent Technologies model 6890 NPD.

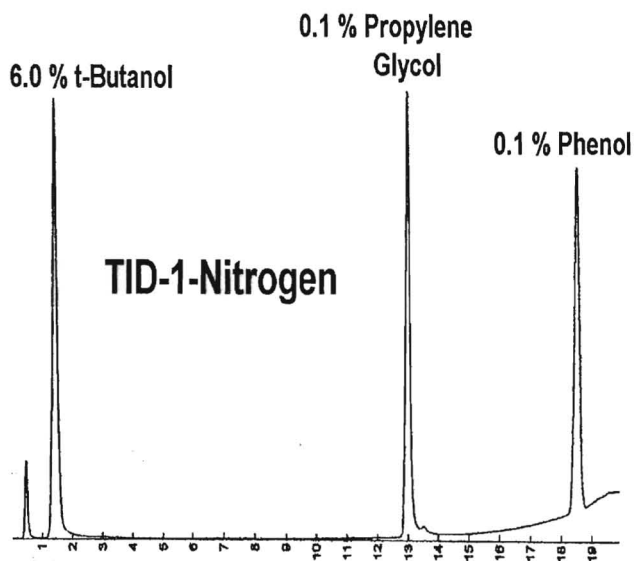
DET Electronic Module.

A DET Detector Current Supply module provides precision control of the heating current for the ion source, plus a selection of several different polarization voltages for optimizing detector response in all modes of detection. The DET supply is a stand-alone module that is 6 inches wide, 10 inches deep, 5.5 inches tall, and weighs 7.5 pounds. It couples to the SRI GC via a 4 foot long cable. Precision controlled constant heating currents in the range of 0 to 4000 mA are provided to the ion source via a thumbwheel control. A selection of -5, -15, or -45 Volts polarization between the ion source and collector electrode is also provided. -5 V polarization is used for NP detection, whereas -45 V is used for best response to Oxygenates.

EXAMPLES OF SELECTIVE DETECTION WITH A COMPACT GC

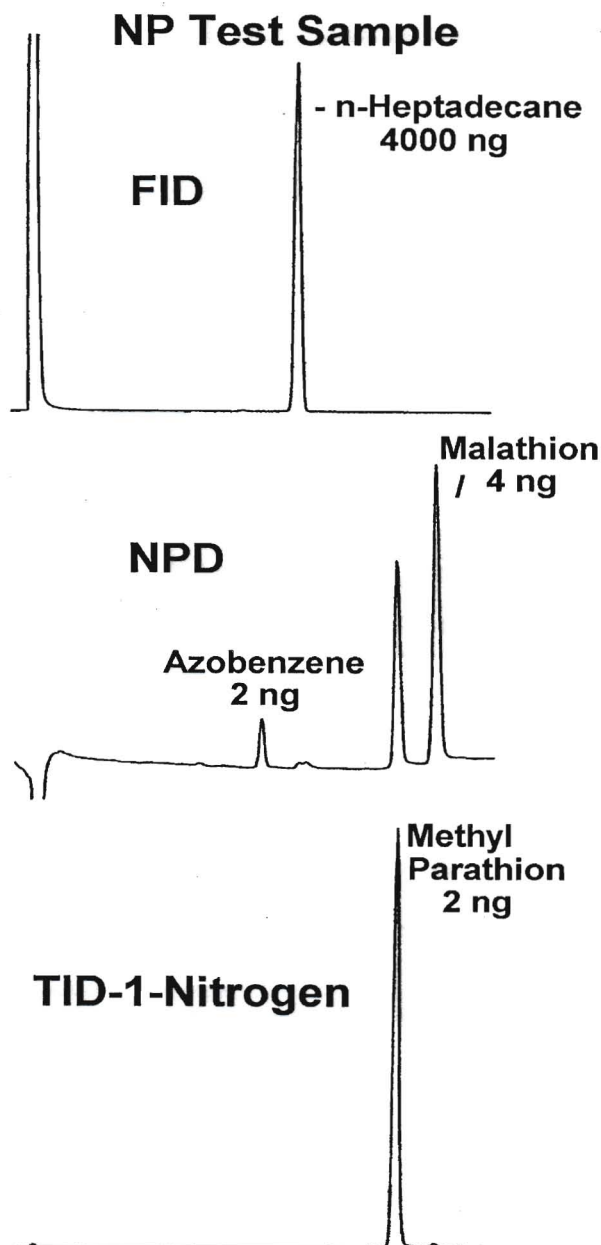


ETHANOL IN GASOLINE. Ionization on a TID-1 ceramic surface provides excellent selectivity for detection of Ethanol amidst the many Hydrocarbon components of gasoline. A single Nitrogen gas suffices as both carrier and detector gas. For these data, a 0.3 μ L sample of a commercial gasoline was injected into the 185°C glass insert of the flash vaporization injector. The column was a 15 m x 0.53 mm x 5.0 μ m MXT-1 type. Column temperature program was 45°C - 1.5 min, 45 - 205°C at 20°C/min, 205°C - 2 min. The carrier gas was also pressure programmed at 9.0 psi - 1.5 min, 9.0 - 11.1 psi at 0.267 psi/min, 11.1 psi - 2 min. Due to the excellent selectivity of TID-1 ionization, there was no need to chromatographically separate overlapping Hydrocarbon peaks. However, to prevent buildup of sample components on the column, the total analysis time of 11.5 minutes was used, although the Ethanol peak eluted within the first minute. Detector temperature was 270°C. For the TID-1 data, N₂ was supplied at 8 psi through the "H₂" labeled detector gas line, and at 2 psi through the "Air" labeled detector gas line. Heating current to the TID-1 ion source was 2.50 A, and the polarization was - 45 V. FID data were obtained by replacing the TID-1 ion source with an FID Ignitor/Polarizer Probe element, and by supplying H₂ at 35 psi and Air at 5 psi to the detector. The FID flame was ignited by raising the heating current to 3.10 A. Once flame ignition occurred, the heating current through the FID probe was reduced to zero. FID polarization was - 45 V.



LARGE RESPONSES TO GLYCOLS AND PHENOLS. TID-1 ionization responses to some Oxygenate classes are substantially bigger than others, although all have good selectivity versus Hydrocarbons. Two classes with especially large responses are Glycols and Phenols. These data demonstrate that a sample containing 0.1 % concentrations of Propylene Glycol and Phenol in an iso-Octane solvent, produced TID-1 responses for those compounds which were similar in magnitude to a much higher 6 % concentration of t-Butanol. Carboxylic Acids, Vanillin, and Methyl Salicylate are examples of other Oxygenates having large TID-1 responses, while Aldehydes, Ketones, Esters, and Phthalates have responses comparable to that of Alcohols. Column was a 30 m x 0.53 mm x 2.0 μ m MXT-Wax, temperature programmed at 50°C - 2 min, 50 - 190°C at 8°C/min, 190°C - 1 min. Helium was the carrier gas programmed at 20 psi - 2min, 20 - 34 psi at 0.8 psi/min, 34 psi - 1 min. Detector gas was Nitrogen supplied at 2 psi and 8 psi through the "Air" and "H₂" detector lines. Injector = 190°C, detector = 250°C, and TID-1 source heat = 2.60 A.

EXAMPLES OF SELECTIVE DETECTION WITH A COMPACT GC



NP PESTICIDES. One of the main applications of an NPD is the detection of trace level pesticides. The present equipment provides that NP selective capability in a compact GC package. The sample analyzed here was Varian's TSD (i.e., NPD) test sample (Varian part 82-005048-04). This is the standard used at DET for final testing all ceramic coated NP and TID-1 ion sources. It contains 2 ng/ μ L of Azobenzene as a representative N compound; 2 ng/ μ L of Methyl Parathion and 4 ng/ μ L of Malathion as representative Organophosphorus pesticides; and 4000 ng/ μ L of n-Heptadecane as a representative high concentration Hydrocarbon. At the sensitivities displayed in the 3 chromatograms, an FID showed a response only for the Hydrocarbon; an NPD showed responses to the N and P components with only minimal response to the Hydrocarbon; and the TID-1 detector responded to only the Methyl Parathion component.

GC Conditions. 15m x 0.53mm x 5.0 μ m MXT-1 column. Temperature program = 170 - 230°C at 10°C/min, 230°C - 1 min. Helium carrier gas program = 8 - 10 psi at 0.333 psi/min, 10 psi - 1 min. Injector = 220°C, detector = 275°C.

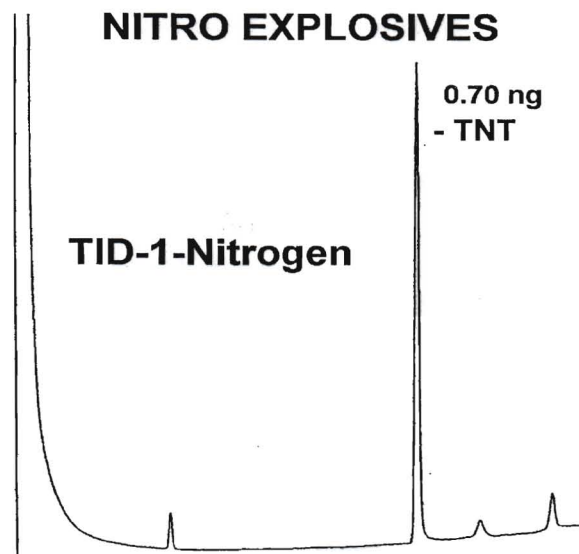
FID Data. Hydrogen = 35psi, Air = 5 psi. FID Ignitor/Polarizer Probe heated to 3.100 Amps to ignite flame, then reduced to 0 A. Polarization = - 45V.

NPD Data. Hydrogen = 7psi, Air = 2 psi. Ceramic TID-2 type ion source used. Source heat = 3.080 A supplied continuously to maintain ignited Hydrogen-Air boundary layer chemistry around the ion source surface. Source polarization = - 5 V.

TID-1 Data. Nitrogen through "H₂" line = 7 psi, Nitrogen through "Air" line = 2 psi. Ceramic TID-1 ion source used at 2.500 A heating current and - 45 V polarization. Large selective response to Methyl Parathion is due to the presence of a strong electronegative NO₂ functional group in a para location relative to other functionalities in that molecule. For similar type compounds, TID-1 ionization provides better selectivity and detectivity than an NPD.

EXAMPLES OF SELECTIVE DETECTION WITH A COMPACT GC

NITRO EXPLOSIVES

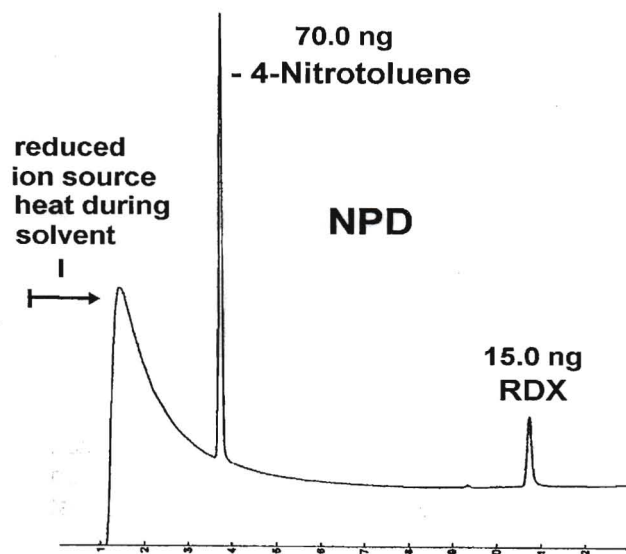


NITRO EXPLOSIVES. Both the NPD and TID-1 modes of detection can be applied to the detection of trace levels of Nitro Explosives in environmental samples. The sample analyzed here was a mixture of 70.0 ng of 4-Nitrotoluene, 0.70 ng of TNT, and 15.0 ng of RDX in a solvent consisting of 93 % Methanol and 7 % Acetonitrile. The data demonstrate the exceptional sensitivity of TID-1 detection for the molecular structure of TNT versus the other two Nitro compounds. In contrast, the NPD provides a more uniform response to all three Nitro compounds, but its detectivity for TNT is not nearly as good as the TID-1 mode.

GC Conditions. 15m x 0.53mm x 5.0µm MXT- 1 column. Temperature program = 120 - 220°C at 8°C/min, 220°C - 2min. Helium carrier gas pressure program = 7 - 10.2 psi at 0.26 psi/min, 10.2psi - 2 min. Injector = 220°C, detector = 270°C.

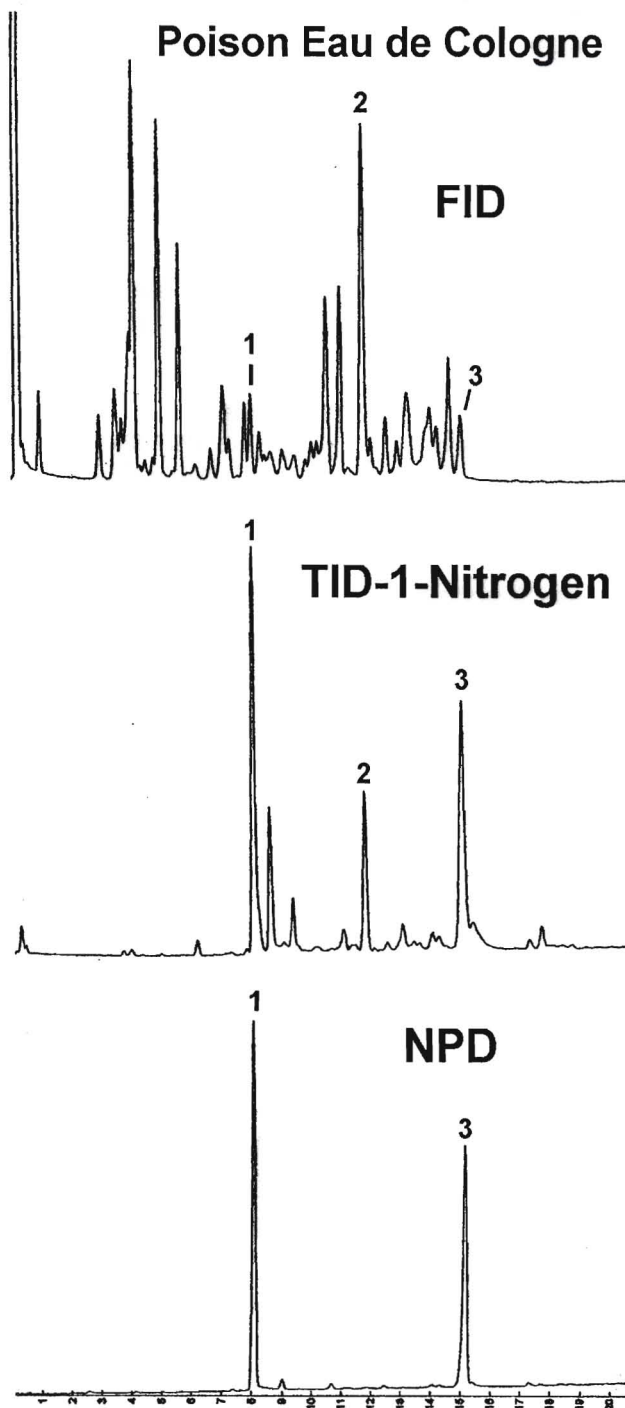
TID-1 Data. Nitrogen through "H₂" line = 8 psi, Nitrogen through "Air" line = 2 psi. TID-1 source heat = 2.550 A, polarization = - 45 V.

NPD Data. Hydrogen = 8 psi, Air = 2 psi. TID-4 type ion source heat = 3.050 A, polarization = - 5 V.



The large Acetonitrile component of the solvent presented an added complication for this sample since both the NPD and TID-1 respond to the Acetonitrile. The NPD chromatogram illustrates a method of dealing with an overly responsive solvent component. This involved extinguishing the H₂ - Air chemistry just prior to injection by reducing the ion source heating current from 3.050 A to 2.050 A, and resetting to 3.050 A at 1 minute into the chromatogram after most of the Acetonitrile had eluted through the detector. This reduction of source heating current during solvent elution is easily accomplished with the thumbwheel adjustment of source heating current on the stand-alone DET Current Supply module.

EXAMPLES OF SELECTIVE DETECTION WITH A COMPACT GC



FRAGRANCES. This analysis provides a good example of the selectivity provided by TID-1 and NPD detection versus an FID detector. The sample analyzed was the commercial fragrance, Poison Eau de Cologne (Christian Dior, Paris). Amongst the numerous peaks exhibited in the FID chromatogram, both the TID-1 and NPD detectors selectively responded to just a few of the sample components.

Unlike the FID and NPD where the sample is consumed in the detector's reactive gas phase H_2 - Air chemistry, the TID-1 detector is non-destructive to sample components. Consequently, aromas of the different fragrance components of this sample could be sensed at the exit of the TID-1 detector, even at retention times when the detector itself was not producing any measurable signal for the component eluting from the column. Hence, during the evolution of the TID-1 chromatogram, it was possible to associate specific aromas with many of the peaks known to be present from the FID chromatogram.

With the present GC system configured originally for either TID-1 or NPD detection, it is easy and inexpensive to convert to the other mode of thermionic detection. In addition, conversion to an FID mode is possible for comparison versus the selective thermionic modes of detection. For users who are interested solely in FID detection with a compact GC, the present system is not very economical. A better choice for those users would be to simply buy the GC and FID from SRI Instruments.

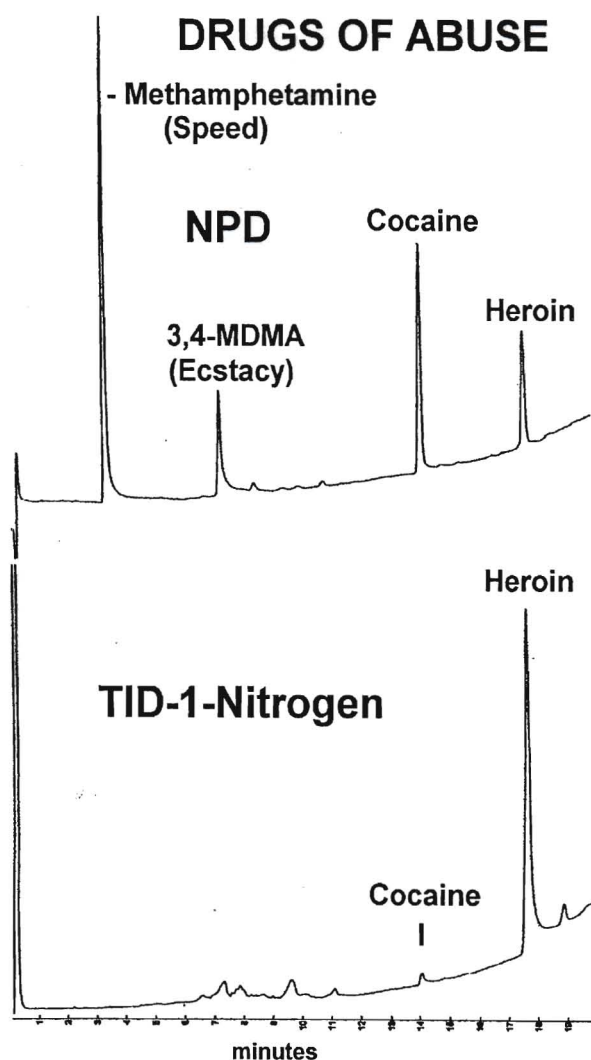
GC Conditions. 15m x 0.53mm x 5.0 μ m MXT-1 column. Temperature program = 60 - 260°C at 10°C/min, 260°C - 3 min. Helium carrier gas program = 13 - 21 psi at 0.4 psi/min, 21 psi - 3 min. Injector = 250°C, detector = 285°C.

FID Data. Hydrogen=35psi, Air=5psi. Flame ignition at 3.400 Amps, then FID Probe reduced to 0 Amps, polarization = - 45 V.

TID-1 Data. Nitrogen through " H_2 " line - 8psi, Nitrogen through "Air" line=2psi. TID-1 ion source heat = 2.600 A, polarization = - 45 V.

NPD Data. Hydrogen=8psi, Air=2psi. TID-4 ion source heat=3.160 A, polarization = - 5 V.

EXAMPLES OF SELECTIVE DETECTION WITH A COMPACT GC



DRUGS OF ABUSE. Another important application of NPD equipment is the detection of drugs of abuse. For applications like this where only compounds containing N atoms are of interest, DET provides an exclusive TID-4 type ceramic ion source which is formulated to provide the best possible N response. This ion source produces more tailing of Phosphorus peaks than a TID-2 type source, so it is not recommended for applications where both N and P detection are required. These data compare the responses of NPD (TID-4) and TID-1 ionization for a sample containing 12 ng each of Methamphetamine, Ecstasy, Cocaine, and Heroin in a Methanol solvent. The NPD detected all four drug compounds, while TID-1 detection provided selectivity for just the Heroin.

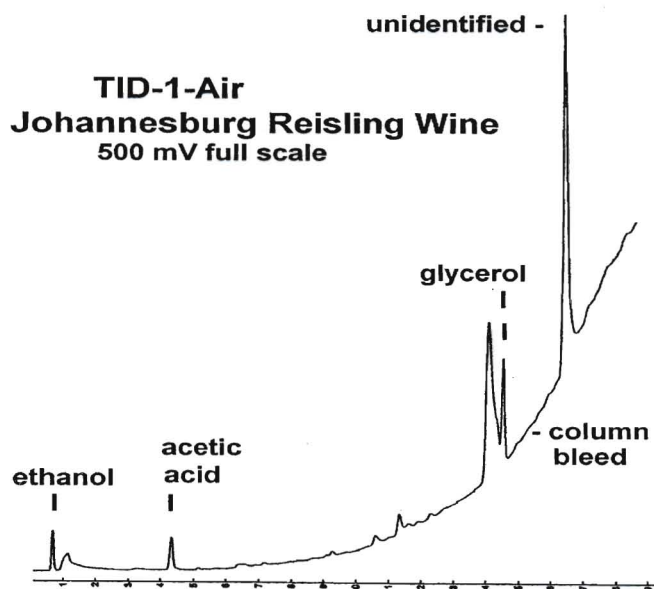
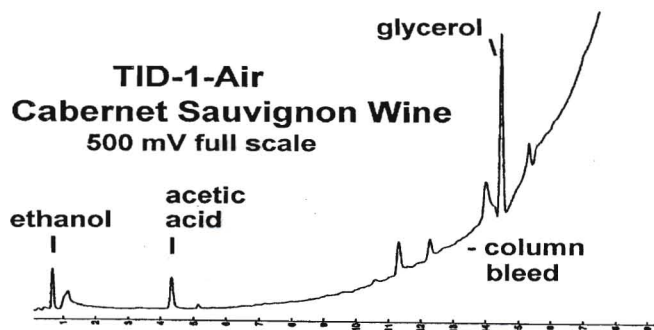
GC Conditions. 15m x 0.53mm x 5.0µm MXT-1 column. Temperature program = 100 - 290°C at 10°C/min, 290°C -1min. Helium carrier gas program = 13 - 20 psi at 0.37 psi/mi, 20 psi - 1 min. Injector = 280°C, detector = 300°C.

NPD Data. Hydrogen = 8 psi, Air = 2 psi. Ceramic TID-4 type ion source used. TID-4 source heat = 3.050 A, polarization = - 5 V.

TID-1 Data. Nitrogen through "H₂" line = 8 psi, Nitrogen through "Air" line = 2 psi. TID-1 source heat = 2.60 A, polarization = - 45 V.

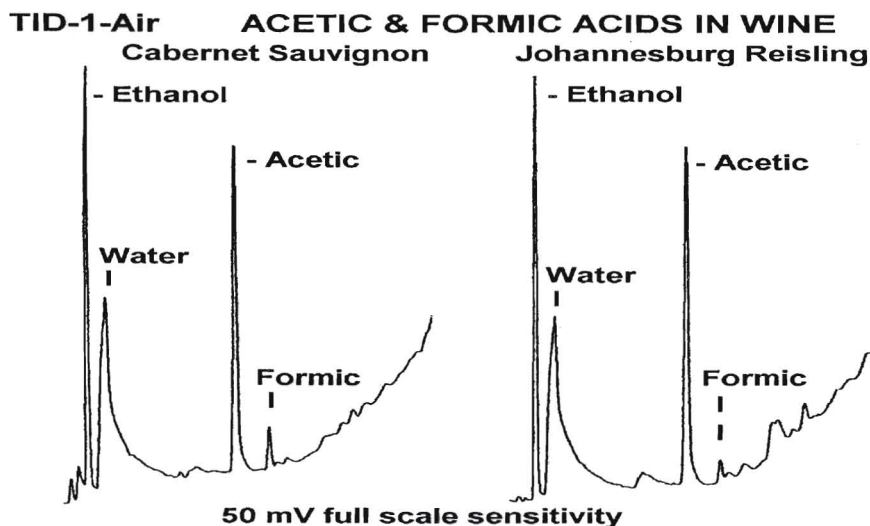
Aside from the different ceramic coating formulations for the ion sources, a major difference between the NPD and TID-1 modes of detection is the existence of the ignited H₂ and Air chemistry in the NPD. This gas phase boundary layer of highly reactive species causes decomposition of sample compounds into products which ultimately extract electrons from the hot surface to form the detected negative ion current. As a result of this decomposition chemistry, the NPD provides general response to most organic compounds containing N or P atoms, irrespective of the original molecular structure of the compound. In contrast, in TID-1 detection, there is only direct ionization by impact of the sample on the ion source surface with no intervening gas phase chemistry. Hence, TID-1 detection is much more dependent on the detailed molecular structure of the sample molecule, and especially on the existence of electronegative functionalities within that structure.

EXAMPLES OF SELL



GLYCEROL IN WINE. TID-1 response to Alcohols is largest when Nitrogen is supplied as the detector gas. When Air or Oxygen are supplied as the detector gas, Alcohol responses are diminished even more relative to high responding oxygenates like Glycols, Phenols, and Carboxylic Acids. This characteristic is especially useful in analyses of alcoholic beverages like wine. These data illustrate the detection of Glycerol in two different wine varieties. 1.6µL of each wine was injected into a 240°C glass liner of the injector. The column used was a 30m x 0.53mm x 2.0µm MXT-Wax, with a temperature program of 100 - 240°C at 8°C/min, 240°C - 1 min. The carrier was pressure programmed at 21 - 35 psi at 0.8 psi/min, 35 psi - 1 min. TID-1 ion source heat = 2.65 A. The column temperature program pushed the upper limit of the Carbowax® polyethylene glycol column coating, and there was a significant column bleed contribution at the end of the chromatograms. This was undoubtedly enhanced by the fact that TID-1 ionization provides excellent detection for Glycols.

ACETIC AND FORMIC ACIDS IN WINE. When the early segments of the Cabernet Sauvignon and Johannesburg Reisling chromatograms are amplified as shown below, peaks for Acetic and Formic Acids are clearly indicated. One of the attributes of TID-1 detection is that it detects Formic Acid, whereas an FID detector does not. Another attribute is that TID-1 detection is not destructive, so aromas of sample constituents can be sensed by a sniffing tube extending from the detector exit port out the top of the GC package.



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This is a universal thermionic detector power supply that can also be used in conjunction with NPD equipment on the Agilent Technologies 6890 GC to provide better response stability with time, plus the capability of easily changing the 6890 NPD to other modes of thermionic detection.

Selective Detection of Oxygenates and Nitro-Compounds. For this detection, DET's TID-1 type ceramic ion source is used in the detector structure, and either Nitrogen or Air are supplied via a gas tee to the "H₂" and "Air" detector gas inlets on the GC. A Nitrogen detector gas environment normally provides the best discrimination versus Hydrocarbon compounds, while an Air environment can be used to suppress responses from certain classes of Oxygenated compounds relative to others. Phenols, Carboxylic Acids, Glycols, Vanillin, and Methyl Salicylate are known to provide especially large TID-1 ion signals in comparison to Alcohols, Aldehydes, Ketones, and Phthalates. All these Oxygenates are detected with good selectivity versus Hydrocarbons. In comparison to other Oxygenates, Ethers (e.g., MTBE) are known to have very small TID-1 responses. Very, very large TID-1 responses are obtained for Nitro compounds like TNT, Methyl Parathion, and 4-Nitrophenol which have a strong electronegative NO₂ functional group located in a para location relative to other functionalities on a Benzene ring.

TID-1 detection is compatible with either He or N₂ as the GC carrier gas. In applications where N₂ carrier provides adequate chromatographic separation, there is the advantage that both carrier and detector gases can be the same single gas supply. One notable feature of TID-1 detection is that it is nondestructive, so aromas of different chemical compounds can be sensed at detector exit tubing extending out the top of the GC package. Possible applications of this compact GC with TID-1 detection include the selective detection of Ethanol in Gasoline; high sensitivity to TNT and 2,4-Dinitrotoluene versus other explosives; high sensitivity and selectivity to nitro pesticides like Methyl Parathion; excellent selectivity for detecting Heroin amongst other drugs of abuse; and detection of Acetic and Formic Acids in Wine.

Selective Detection of Nitrogen-Phosphorus Compounds. NP detection requires supplies of Hydrogen and Air to be connected to the GC in addition to the column carrier gas. DET manufactures 2 types of ceramic ion sources for use in NP detection. One is a Black Ceramic, TID-2 type ion source, which has a surface formulated to

provide sharp Phosphorus peaks. TID-2 is recommended for user's requiring P or both P and N detection (e.g., pesticides). A second White Ceramic, TID-4 type ion source, is formulated to provide the best possible N response at the sacrifice of some tailing of P peaks. TID-4 is recommended for users requiring only N detection (e.g., drugs of abuse). Both of these NP ion source types are identical to ion sources used widely on the Agilent Technologies 6890 NPD.

Easy and Inexpensive Conversion from One Detection Mode to Another. A GC system originally configured for either Oxygenate or NP detection, can be adapted to the other mode of selective detection by simply replacing the ion source (cost \$285), and by plumbing in the appropriate detector gases. Some of the accompanying application illustrations also demonstrate that universal FID detection is possible by replacing the ceramic ion source with a bare wire FID ignitor/polarizer element. Selective detection of volatile Halogenates is also a possibility with a ceramic coated TID-3 type ion source.

Part Numbers/Prices:

- 001-931-11, Oxygenates/Nitro Analyzer, \$13,200.** includes TID-1 ion source, gas fittings for same gas through 2 detector gas lines as well as carrier gas; 15m x 0.53mm MXT-1 column or equivalent; power strip for 115 Vac.
101-931-11, NPD (TID-2) Analyzer, \$13,200. includes TID-2 ion source for P and/or both N and P; 15m x 0.53mm MXT-1 column or equivalent; 115 Vac power strip
501-931-11, NPD (TID-4) Analyzer, \$13,200. Same as above except includes TID-4 ion source for best N signal.

Interchangeable Ion Sources:

- 010-901-00, TID-1 Ceramic Ion Source, \$285.** use with N₂ or Air detector gases, provides selective response to Oxygenates and Nitro compounds.
010-902-00, TID-2 Ceramic Ion Source (NPD), \$285. requires H₂ and Air detector gases, provides selective response to N or P compounds with very sharp P peaks.
010-904-00, TID-4 Ceramic Ion Source (NPD), \$285. requires H₂ and Air detector gases, provides NP selectivity with best possible N response.
020-902-00, FID Ignitor/Polarizer Probe, \$195. requires H₂ and Air detector gases, provides universal Hydrocarbon response.
010-903-00, TID-3 Ceramic Ion Source, \$285. use with N₂ or Air detector gases, provides selective detection of volatile Halogenates such as Trihalomethanes.