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Figure 8 shows a comparison of NPD and TID-1 chromatograms for a sample containing 8.5 ng of Nitroglycerine, 25 ng of PETN, and 0.50 ng of RDX. The TID-4 ion source used for the NPD data was the same source used earlier for Figure 3 (i.e., source had 750 hours prior use). It's clear from Figure 8 that the NPD provides excellent response to RDX in comparison to the other 2 compounds in the sample, while TID-1 response to RDX appears to be similar to its response to the other compounds. For both NPD and TID-1, the detector noise (about 0.013 pA) was just slightly greater than the electrometer noise. From the signal magnitudes in Figure 8, the NPD compound detectivities (i.e., 3 times noise level) were calculated to be 0.74 pg for RDX, 140 pg for Nitroglycerine, and 180 pg for PETN. TID-1 detectivities for PETN and

Nitroglycerine were about 2 times higher than the NPD detectivities for these compounds.

The 2 peaks labeled U 1 and U 2 in Figure 8 were impurities present in the sample mixture. It's interesting that U2 appeared in the TID-1 chromatogram, but not in the NPD chromatogram. Conversely, U1 appeared in the NPD chromatogram but not in the TID-1 chromatogram. This is a good illustration how sensitive, selective detectors can often reveal trace sample constituents that might otherwise be missed with other detector types. In the case of the U2 component, it's evident from the TID-1 data in Figure 7 that it was an impurity in the PETN standard that was used.

3.) FID, NPD, AND TID-1 TRANSDUCERS FOR REAL TIME MONITORING OF SAMPLES IN AN AIR STREAM.

Previous DET Reports have addressed the use of thermionic detectors like the NPD and TID-1 in stand-alone applications involving samples in an Air stream. Although these reports described detector hardware configurations that did not include a GC installation, they still included some means of providing external heating control of the detector body. However, DET detection transducers designed for stand-alone applications are small enough in physical size that some self-heating occurs from the detection mechanism operating within the transducer body. The present report describes using FID, NPD, and TID-1 transducers that had only a simple thermal wrap covering and no other external heat.

DET's experience of designing detectors to fit different brand GC instruments has led to a methodology for constructing detection structures with many different tube or Swage type inlet and outlet configurations. As a consequence, these detection structures or transducers can be easily mated to standard type gas line fittings. DET transducer bodies are constructed of stainless steel and ceramic materials so they are capable of withstanding operation up to 400°C.

Since Air is a primary detector gas supplied to thermionic detectors like the NPD or TID-1, as well as to an FID, it is a logical extension to consider using these detector types to sense samples carried in the Air stream rather than in an inert carrier gas stream

eluting from a GC column. In the present work, the Air supply to the FID, NPD, or TID-1 transducers was simply ambient Air drawn into the transducer by attaching a sampling pump to the transducer's exit port. For gathering data, the transducers were simply supported on a laboratory ring stand, and connected to the appropriate stand-alone power and signal electronics.

FID Transducer for Samples in an Air Stream. In the conventional implementation of Flame Ionization Detection, samples are admixed with Hydrogen and enter the flame through the center orifice of a jet structure, and Air is supplied around the outer periphery of the jet. In this manner, it is ensured that all the sample passes through the very core of the flame. With samples introduced with the Air supply around the outer periphery of the jet, it is clear that some sample molecules will likely bypass the actual flame. Hence, it is to be expected that an FID with sample compounds in the Air stream will not be quite as sensitive as the conventional FID with samples in the interior of the flame.

Hydrogen-Air flames are unique chemical environments characterized by high temperatures and high concentrations of radical or unstable chemical species such as H, O, and OH. Sample molecules are efficiently decomposed in such a reactive environment, and sample fragments are ionized in gas phase

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reactions with the flame radicals. For organic samples, an important mechanism is the chemi-ionization reaction $\text{CH} + \text{O} = \text{CHO}^+ + \text{e}^-$. This ionization occurs in that flame region where the CH and O radicals are at their highest concentrations, and that is the conical periphery of the flame where the Hydrogen and Air are mixing together. In a conventional FID design, a very small orifice jet is preferred in order to provide a tall thin flame where the ionization region is constricted as small as possible to the flame core. For an FID where samples are in the Air stream, a short broad flame is more desirable in order to have the ionization region extend out into as much of the Air stream as possible.

Figure 9 shows a schematic of the FID transducer used in this work. The jet was a ceramic tube of 0.125 inches O.D. x 0.062 inches I.D., and that was surrounded by an ion collector cylinder of 0.200 inches inner diameter. The collector electrode was insulated from the surrounding transducer body by a high purity alumina ceramic sleeve. A Bare Wire loop located downstream of the jet served the dual role as Flame Ignitor and Polarizer. The mounting flange for the Ignitor/Polarizer element was identical to that used on DET and Agilent 6890 NPD ion sources. Power for the Bare Wire FID Probe and signal measurement from the ion collector were provided by a DET Current Supply/Electrometer module.

FID TRANSDUCER FOR SAMPLES IN AIR

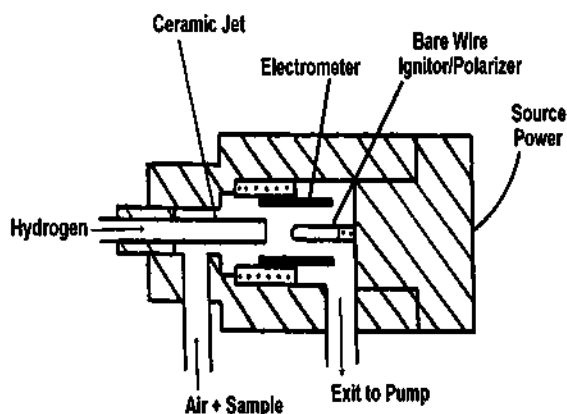


Figure 9. Schematic of FID Transducer for Air samples.

The FID Transducer body incorporated a 1/8 inch Swagelok seal for the jet attachment, a 1/4 inch tube for the incoming Air and sample, and a 1/4 inch tube for the exit port. The jet was connected to a Hydrogen inlet line via a 1/8 to 1/16 inch Swagelok reducer, and the interior of the Air inlet tube had a glass wool packing to prevent detector spikes from incoming particulate matter. Hydrogen flow was provided by a DET Flow Control module which included an adjustable needle flow restrictor and on/off control without changing the flow setting. A calibration of flow versus gas supply pressure was used to determine the Hydrogen supplied to the FID as well as to an NPD transducer. For the FID data of this report, the Hydrogen flow was 30 mL/min.

In attaching a sampling pump to the exit of an FID transducer, consideration must be given to handling the potential condensation of Water vapor produced by the flame. Once the flame is ignited, the transducer body self heats in about 15 minutes so that condensation within the transducer no longer occurs. However, condensation can occur in the unheated tubing leading to the pump. To avoid this, we attached a gas tee configuration at the transducer exit, and used a 5 L/min pump to pull a 0.5 L/min Air sample through the transducer, and an additional 4.5 L/min Air purge through the exit tee. This purge gas eliminated condensation in the gas lines to the pump.

Figures 10 -13 illustrate data obtained with the FID Transducer. After first ignition of the flame, we allowed 45 minutes for thermal equilibration of the transducer and for all traces of moisture to be eliminated from inside the detector volume. Various types of samples were then brought to the vicinity of the transducer inlet to allow their organic vapors to be swept in with the ambient Air pulled into the transducer.

Figure 10 shows signals obtained from an open vial of iso-Octane, and from a small injection of Methane into the ambient Air located about 1/4 inch away from the transducer inlet. Figure 11 compares signals for vapors emanating from liquid samples of Scotch Whiskey (i.e., Ethanol response), and a 0.1% solution of Volatile Fatty Acids in Water. Also shown in Figure 11 is the signal obtained from vapors emanating from a solid sample which consisted of the very aromatic leaves of a Herbal Tea (i.e., Good Earth brand). The large Tea Leaves signal was further compared in Figure 12 with signals from Ground Coffee and

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Coffee Beans. Figure 12 also shows signals generated from Human Breath samples exhaled and inhaled through a tube that terminated at an ambient Air exit location about 1/4 inch in front of the transducer inlet.

In order to ignite the FID flame initially, an electrical current was passed through the Bare Wire element to raise its temperature sufficiently for ignition. Once the flame was ignited, this heating current was reduced to zero, and the Bare Wire element then served as just a - 45 V polarizer to drive negative ions in the flame toward the collector electrode. However, once the transducer body heated up from the flame, we discovered that the flame autoignited with just the turn on of Hydrogen flow and no additional heating current applied to the Bare Wire. This effect is illustrated in Figure 13. The autoignition was attributed to catalytic processes occurring at the Bare Wire surface.

Also shown in Figure 13 is a comparison of signals from vapors evolved from a 1 gm Soil sample versus a similar Soil sample Spiked with 3 µL of Diesel Fuel. For these data, the solid soil samples were distributed inside the bottom of a 50 mL open top vial and vapors at the top of the vial were sniffed by the FID Air inlet..

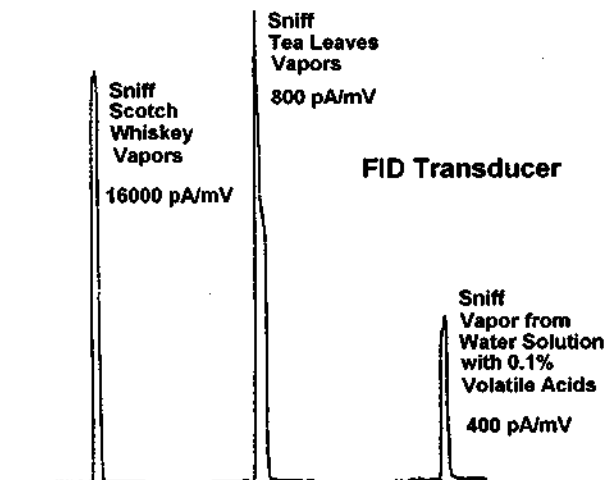


Figure 11.

FID Transducer 400 pA/mV
 hydrogen = 30, air = 500 mL/min

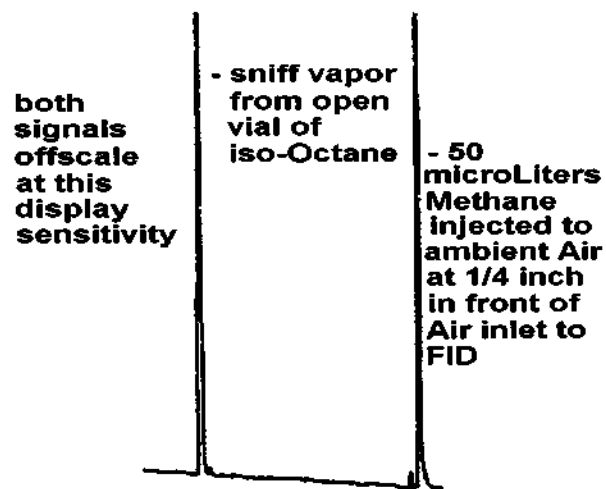


Figure 10.

FID Transducer 320 pA/mV

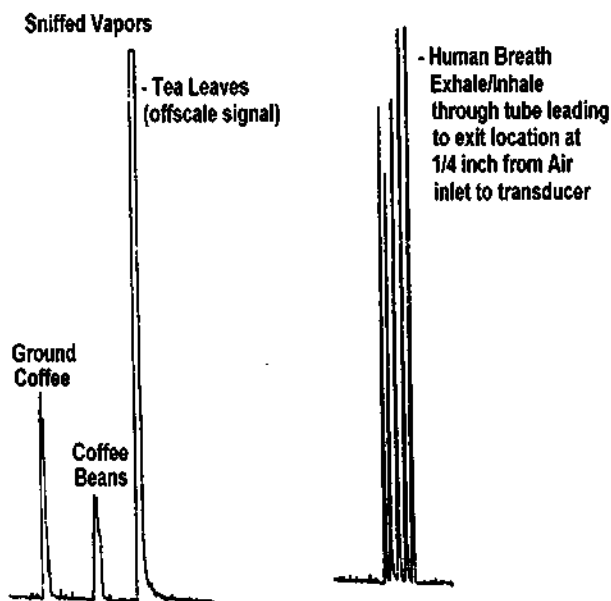


Figure 12.

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FID Transducer

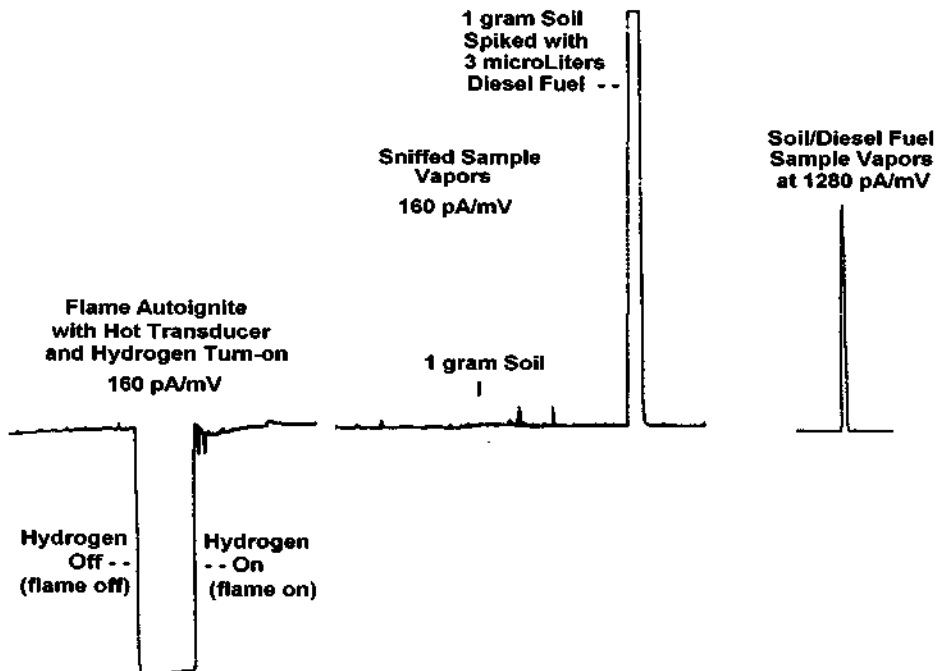


Figure 13. Demonstration of flame autoignition with just turn on of Hydrogen and no electrical heat applied to ignitor wire. Comparison of signals from soil samples with and without contamination by diesel fuel.

NPD Transducer for Samples in an Air Stream.

Like the FID, an NPD requires the addition of some Hydrogen to the incoming Air flow. However, there is no requirement for a jet structure, so the Hydrogen can simply be added with a gas tee at the transducer inlet. Figure 14 shows a schematic of the NPD Transducer used in this work. The thermionic ion source used in this work was a Black Ceramic TID-2 type. The main transducer body had a 3/8 inch O.D. tube inlet, and that was attached to a 3/8 inch Swagelok union and 3/8 to 1/4 inch Swagelok port reducer tube which provided the Air inlet path. The side of the 3/8 Swagelok union was modified with the addition of a tee connection providing a 1/16 inch Swagelok fitting for the Hydrogen inlet.

Like an FID, the Hydrogen - Air chemistry in an NPD also produces some Water vapor, but at a much lower concentration than the FID. Consequently, it was possible to connect the sampling pump directly to the

1/4 inch Swagelok outlet of the transducer without requiring any additional exit purge gas flow as was used with the FID. For the NPD data of this report, the Air flow was 350 mL/min and the Hydrogen flow was 9.8 mL/min.

NPD TRANSDUCER FOR SAMPLES IN AIR

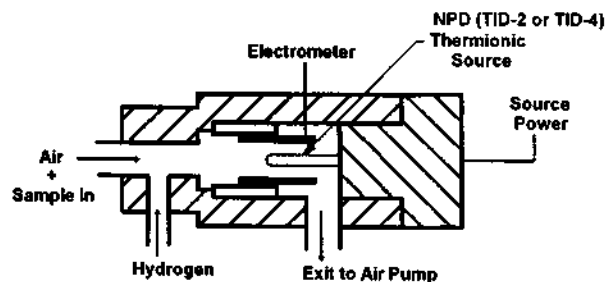


Figure 14. Schematic of NPD Transducer for Air samples.

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NPD Transducer 12800 pA/mV
Hydrogen = 9.8, Air = 350 mL/min
Sniffed Vapors from Open Sample Vials

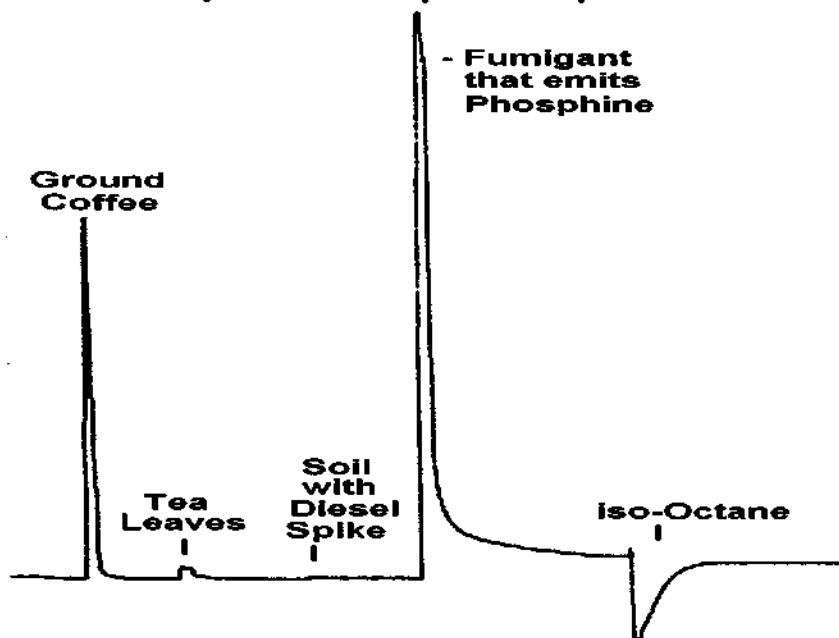


Figure 15.

Figure 15 shows some signals generated with the NPD Transducer. The Ground Coffee, Tea Leaves, and Diesel Soil samples were the same as in the FID data of Figures 12 and 13. In contrast to the FID response, the NPD exhibited a negligible signal for the Diesel Soil sample, and the signal for the aromatic Tea Leaves was small compared to the signal for the N-containing aroma compounds from the Ground Coffee. Meanwhile, a large signal was obtained from the vapors emanating from a Grain Fumigant that emits Phosphine when exposed to moisture. Figure 15 also exhibits a negative signal due to exposure to the vapors from an open bottle of iso-Octane. At high concentrations of Hydrocarbons in the incoming gas stream, the ignited chemistry in the NPD can be quenched as evidenced by a negative type signal.

TID-1 Transducer for Samples in an Air stream.

TID-1 detection is the easiest to implement because it requires only Air as the operating gas. Figure 16 shows a schematic of the TID-1 Transducer used in this work. The transducer body incorporated a 1/8 inch Swagelok

fitting for the Air inlet and a 1/4 inch Swagelok exit port. A 1/8 inch O.D. x 1/16 inch I.D. x 2 inch long tube was attached to the inlet to allow probing of vapors in small spaces. For the data of this report, a pump pulled an Air flow of 600 mL/min through the transducer.

TID-1 TRANSDUCER FOR SAMPLES IN AIR

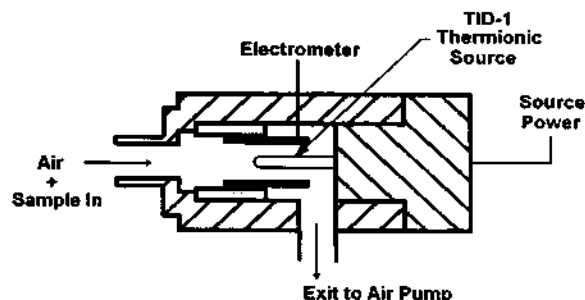


Figure 16. Schematic of TID-1 Transducer for samples in an Air stream.

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TID-1 Transducer

Air = 600 mL/min

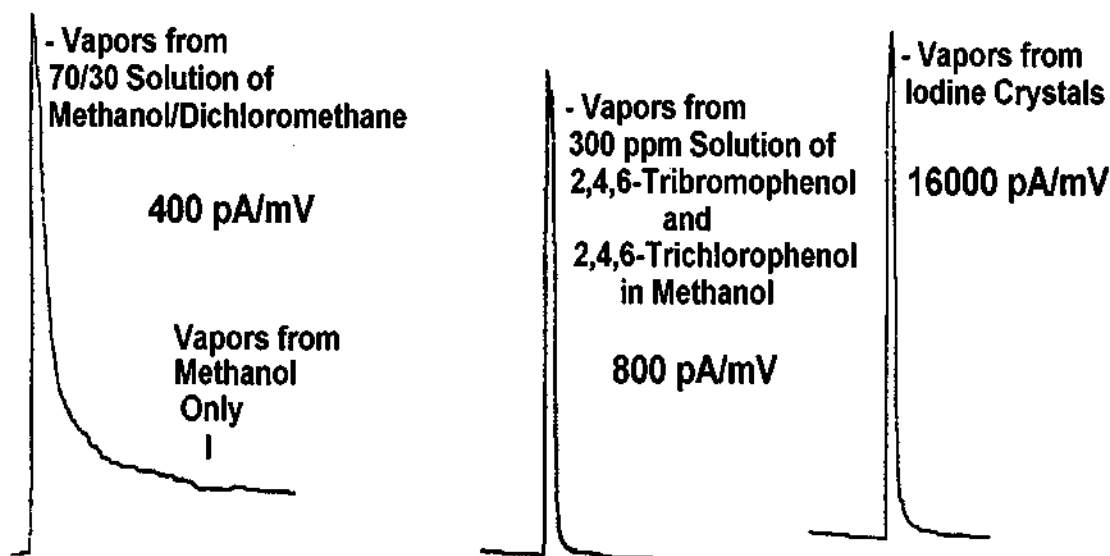


Figure 17.

Figure 17 compares TID-1 signals for several different types of Halogenated samples. For these data as well as for previous FID and NPD data, the transducer inlet was exposed to the sample for a short period of time and the sample was then moved away. This procedure produced peak like signals such as the Iodine or Tribromo/Trichloro-phenol signals. However, exposure to vapors of Dichloromethane produced a longer term "tailing" of the signal peak indicating that this chlorinated sample had temporarily changed the charge emission characteristics of the TID-1 surface, and that effect lingered on for some time after the sample was removed. This is consistent with previous observations of TID-1 detection in GC applications. For sensing Volatile Chlorinated compounds, a TID-3 ion source which operates at a higher surface temperature provides much less tailing (i.e., faster response time).

We have known for some time that Iodine vapors produce an especially large TID-1 signal. From a consideration of the vapor pressure of Iodine at room temperature, and uncertainty of how much Air was

ingested along with the I_2 , we estimate that the TID-1 response in Figure 17 corresponded to an I_2 concentration in the range of 10 - 100 ppm in the incoming Air. Sniffing vapors emanating from a few crystals of Iodine in a vial has proven to be a simple way of determining the magnitude of ion source heating current to use in order to achieve a large TID-1 response.

The large TID-1 signal obtained from the Bromo/Chloro-phenol sample illustrated the good selectivity and sensitivity obtained for these compounds despite the fact that their concentrations in the sampled vapors were much less than the concentration of the more volatile Methanol.

Figures 18 and 19 compare TID-1 responses for vapors emanating from some food products. It was known from previous GC work that TID-1 ionization produced a good response to Vanillin, and that is consistent with the Coffee Bean data in Figure 18. Similarly, it was known previously that the compound

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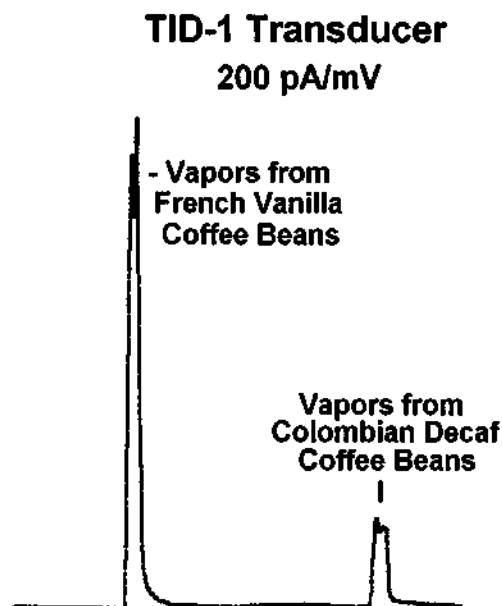


Figure 18.

Allyl Isothiocyanate (i.e., principle component of volatile oil of mustard) produced a large TID-1 response, and that is consistent with the comparison of Mustard samples in Figure 19.

Figure 20 shows a comparison of TID-1 responses to various fragrance essences obtained from Parfumerie Fragonard in France. This demonstrates TID-1 selectivity for detecting certain types of fragrances versus others. Unlike the FID or NPD, a TID-1 transducer is not destructive to the sample compound, so distinctive aromas can be sensed at the exit of the transducer. Also, it is possible to series couple a TID-1 transducer with an NPD or FID transducer to simultaneously generate 2 different detection signals from the same sample.

Summary. The FID, NPD, and TID-1 transducers described in this section were all self-heated and thermally insulated by fiberglass sleeving wrapped in a mummy-like fashion around the transducer body. Air flow through the transducers was provided by attaching a sampling pump to the exit port of the transducer. The magnitude of the Air flow rate through the transducer was determined by the capacity of the sampling pump as well as by the upstream flow

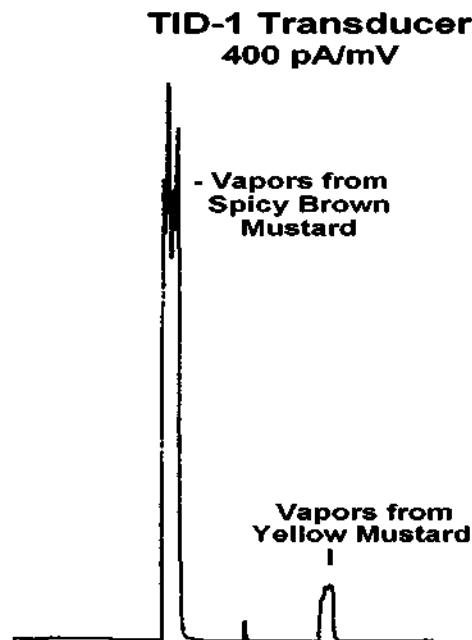


Figure 19.

restrictions such as the size of the inlet tubing or packing of glass wool in the inlet. For the FID transducer, a 5 L/min pump (i.e., Laboport model from KNF) was used, while a 1.5 L/min pump (Schwarzer Prazision) was used with the NPD and TID-1 transducers. To eliminate Water condensation in the pump tubing, the FID transducer had a 1/4 inch Swagelok Tee attached to the transducer exit with a 1/4 x 1/8 inch tube port reducer attached at the tee location. This configuration provided an Air flow of 0.50 L/min through the transducer and 4.5 L/min purge at the transducer exit. The FID, NPD, or TID-1 transducer inlets were either tube or Swage type fittings that could be coupled to standard type gas connections if required.

Power and signal measuring electronics for the transducers was provided by a stand-alone DET Current Supply/Electrometer module. The Current Supply provided both heating currents and polarization voltages for the FID Ignitor/Polarizer Probe, and the TID-1 and TID-2 Thermionic Ion Sources. FID and TID-1 detection used a polarization of - 45 V, while the NPD used a polarization of - 5 V.

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levels increased so that the signal-to-noise is about the same for both sets of data. Generally, the operating lifetime of the thermionic source and the specificity of detection are diminished as the surface temperature is increased further and further. Hence, the general rule-of-thumb is to operate the thermionic source at the lowest heating current compatible with the desired sample detection.

In Figure 5, the I_2 signal response was generated by holding up to the Reactor inlet the open end of a 2mL sample vial containing a few iodine crystals. With an RTIA module drawing in ambient air, this type of sample introduction by "sniffing" volatiles of solid or liquid substances is a simple and quick method of checking sensitivity and specificity of the TID Transducer. Although the absolute concentration of sample introduced is not as well determined as it is with Permeation Tubes, the signals generated are quite reproducible if the sample vial is held each time at the same position relative to the Reactor inlet. Figure 6 illustrates the reproducibility of I_2 signals generated over a one week period of continuous operation.

There is a notation in Figure 4 that the "spikes" observed in the data traces are caused by dust particulates drawn into the TID Transducer through open inlet tubing. Figure 7 illustrates data from a dustier air environment, as evidenced by a much higher frequency of spikes. Figure 7 also illustrates that the spikes are eliminated by packing a small wad of glass wool inside the Reactor Chamber. These observations

suggest that the frequency of spikes in the TID Transducer signal can be used as a qualitative indicator of the number density of dust, pollen, smoke, or other particulates contained in the volumes of sampled air being drawn through the RTIA System.

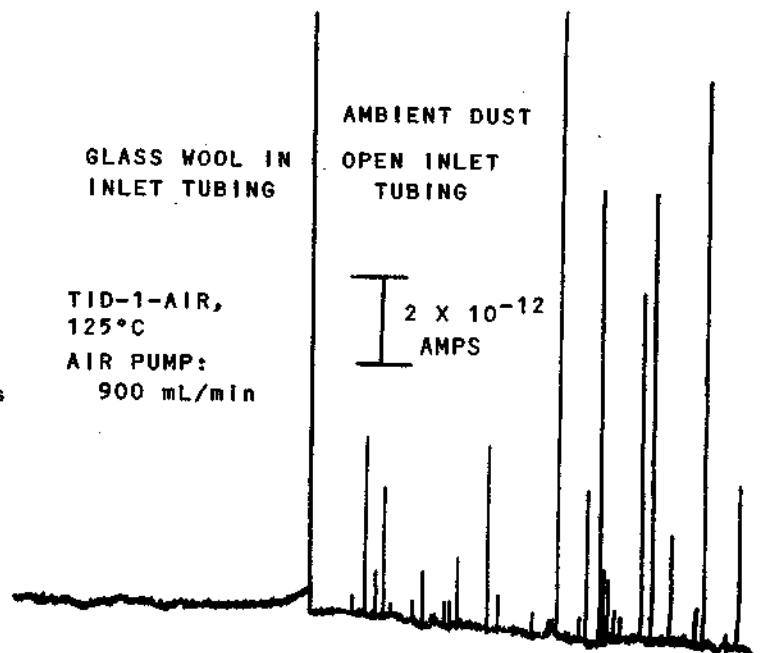
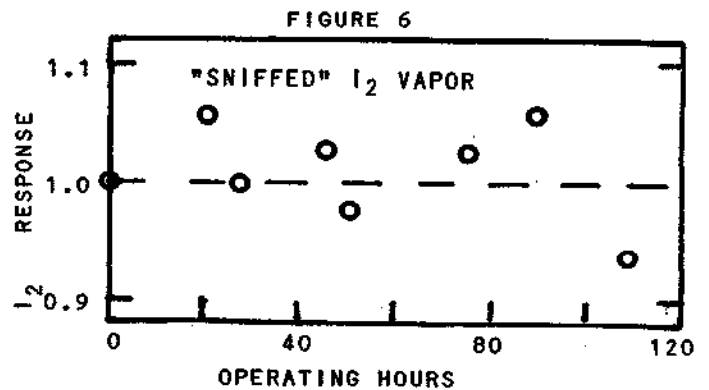


FIGURE 7