Recent Advances in Thermionic Ionization Detection for Gas Chromatography

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Abstract
Thermionic ionization detectors are most widely used for the specific detection of nitrogen-phosphorus compounds in gas chromatography. The operating mechanism of these detectors is a surface ionization process in which the key parameters are the work function of the thermionic emission surface, the temperature of the thermionic surface, and the composition of the gas environment in the immediate vicinity of the thermionic surface. By systematic variations of each of these three key parameters, the technique of thermionic ionization detection has been greatly expanded to encompass a number of different modes of response, all of which use similar detector hardware and electronic components.

Introduction
Thermionic ionization detectors (TID) are best known in gas chromatography (GC) for their application to the specific detection of nitrogen (N) or phosphorus (P) compounds. All modern TIDs are essentially derivations of a basic design first described by Kolb and Bischoff (1) in 1974. The main component in this type of detector is an electrically-heated thermionic emission source in the form of a bead or cylinder which is usually composed of an alkali-metal compound impregnating a glass or ceramic matrix. In the TID, the thermionic source is positioned so that sample compounds may impinge upon its surface, and any ionization produced is measured by an adjacent collector electrode. Kolb and Bischoff were the first to report that a thermionic source comprised of a Rb-silicate glass bead produced very specific NP responses when the bead was operated at high temperatures in a gas environment of dilute H₂ in air.

Since the original work of Kolb and Bischoff, there have been continuing developments in NP detectors, with much emphasis on improved methods of construction and composition of the thermionic emission sources. The most important development, however, has been the recognition in recent years that the operation mechanism of a TID is a surface ionization process (2) rather than the gas phase ionization process originally proposed by Kolb et al. (1,3). Once it was clear that a surface ionization process was operative, it was possible to identify three key operating parameters which control the ionization produced. These parameters are: the electronic work function of the thermionic emission surface which is determined by the chemical composition of the surface; the temperature of the thermionic surface; and the chemical composition of the gas environment immediately surrounding the thermionic surface.

The identification of these parameters has led to a clearer understanding of the complex chemistry active in NP detection, and has provided an important guide for expanding the applications of thermionic ionization techniques. Through systematic variations in each of the key parameters, many different modes of detector response have been achieved (3-6). Hence, the technique of thermionic ionization detection now correctly refers to a number of GC detector responses which are related through the use of many common hardware and electronic components. This article reviews the present state of development of the members of this unique group of detectors.

Types of Thermionic Emission Sources
All commercially available TIDs use thermionic emission sources formed according to one of the following four general methods:
(A) homogeneous alkali-glass bead formed on a loop of bare platinum wire (1);
(B) alkali salt activator coated on a ceramic cylinder core containing an embedded heater coil (7);
(C) homogeneous alkali-ceramic bead formed on a coil of nichrome heater wire (2,8,9);
(D) multiple layers of cylindrically-shaped ceramic coatings, with a non-corrosive, electrically-conducting sub-layer of Ni-ceramic completely covering a loop of nichrome wire, and a surface layer comprised of alkali and/or other additives in a ceramic matrix (5,10).
Thermionic sources representing all four categories cited above have been used in NP detectors available from different manufacturers. Generally, those sources formed from ceramic materials provide greater flexibility for varying the chemical composition of the source. This is because the ceramic compositions are formulated and coated from a slurry at room temperature (9), whereas the glass compositions are formed in
a process that proceeds through a molten glass state (11).

The detailed chemical compositions of thermonic emission sources are usually regarded as confidential proprietary information by the manufacturer. Since the first alkali-glass bead reported by Kolb and Bischoff used Rb as the alkali compound, there existed for many years a belief that Rb was an essential component for optimum NP responses. However, in recent years, NP detectors with state-of-the-art performance specifications have been reported in which Cs rather than Rb is used as the alkali component (5). Also, another recent report (12) has described an NP detector which uses a LaB6 SiO2 bead and no alkali additive. In accordance with a mechanism of surface ionization prevailing in the TID, the most important characteristic of the thermonic emission surface is its electronic work function (i.e., the amount of energy required to emit a unit of electrical charge from the surface). Alkali-metal compounds have been especially successful additives because they lower the work function of the glass or ceramic matrix, thereby facilitating the emission of charged particles from the heated thermonic surface. The mathematical relationships between work function, surface temperature, and thermonic emission current have been discussed (2,12).

The development of multiple-layered, ceramic-coated thermonic emission sources has allowed examination of coatings of many different chemical compositions without the risk of materials in the surface layer corroding the heater wire. In the search for expanded applications for thermonic ionization techniques, the basic task is to define a specific match of a thermonic source type with an operating gas environment and a range of operating source temperatures. To date, three different chemical compositions of thermonic sources have been shown (5,6) to have useful applications in differing modes of thermonic detection. These source compositions are shown in Table 1. Data obtained using these three types of thermonic emission sources are presented in the following sections.

Modes of Response

Schematic illustrations of four different versions of thermonic ionization detection equipment are shown in Figures 1 through 4. Common components in each version as follows: (A) an electrically-heated, thermonic/catalytic source constructed of multiple layers of ceramic coatings; (B) a cylindrical collector electrode surrounding the cylindrically shaped thermonic source; (C) a source power supply that provides heating current to heat the source to typical temperatures of 400° to 800°C, and a bias voltage to polarize the source structure at a negative voltage with respect to the collector;

(D) an electrometer that measures negative ionization currents arriving at the collector electrode.

The TID hardware usually mounts onto an FID-type detector base that is resident on a GC, so that two different detector gases may be supplied in addition to the GC effluent. Therefore, changes in the modes of detector response that correspond to the schematics of Figures 1 through 4 are accomplished by changes in the type of thermonic source, changes in the composition of gases supplied to the detector, or by changes in the operating temperature of the thermonic surface.

Most of the TIDs available commercially function by the collection of negative ionization rather than positive ionization. In the discussion that follows, it will be shown that the concepts of negative ion chemistry provide a logical pattern for correlating the responses of the different modes of thermonic detection.

TID-1-N2: Nitro/electron negative specific response

The simplest mode of thermonic detection is represented by the schematic in Figure 1. In this mode, the low work function thermonic source designated by the TID-1 nomenclature is operated in a detector gas environment of N2. Because the detector gases are inert, sample compounds interact directly with the TID-1 surface, which is typically heated to temperatures in the range of 400° to 800°C. The ionization process in this case is direct transfer of negative charge from the TID-1 surface to

<table>
<thead>
<tr>
<th>Table 1. Thermionic Source Surface Layers</th>
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<tr>
<td>Source type*</td>
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<tr>
<td>-----------------------------------------</td>
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<tr>
<td>TID-1</td>
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<tr>
<td>TID-2</td>
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<tr>
<td>CFID</td>
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*Nomenclature adapted from Patterson (5).

Figure 1. Schematic illustration of the detection configuration for the thermonic ionization modes TID-1-N2 and TID-1-air. Detector gas 1 = FID-H2 inlet line; detector gas 2 = FID-air inlet line.
the sample molecule. Consequently, this mode of response provides exceptionally high specificity and sensitivity to many compounds containing the nitro (NO$_2$) functional group (5,13), as well as to certain other electronegative compounds (e.g., pentachlorophenol, diazepam, and methaqualone). This mode of detection is very sensitive to the detailed electronegativity of the sample's molecular structure, as has been illustrated by the observation that a larger signal is obtained for the 2,4-isomer of dinitrotoluene in comparison to the 2,6-isomer (5). The TID-1-N$_2$ mode is superior to a conventional NP detector or an electron capture detector (ECD) for detection of trace level nitro-compounds such as nitro-PAH, nitro-explosives, nitro-pesticides (e.g., parathion, methyl parathion), nitro-drugs, nitro-derivatives. For many nitro-compounds, the specificity vs. hydrocarbons is an astonishing 10$^6$, and detectivity is in the 0.1- to 1.0-ng range (5).

**TID-1-air: Halogen/nitro specific response**

When the TID-1 thermionic source is operated in an oxygen-containing gas environment rather than one of N$_2$, specific responses to halogenated compounds are enhanced while responses to nitro-compounds are decreased somewhat (14). The TID-1-air mode of detection is generally not as sensitive as an ECD or Hall detector for chlorinated compounds, but it provides halogen specificity at higher concentrations where ECD and Hall are saturated. Typical specificity is 10$^6$ and detectivity is 0.1 to 1.0 ng. This is an especially simple mode of detection for ethylene dibromide (EDB) in the headspace vapors of food products.

**TID-2-H$_2$/air: Nitrogen/phosphorus specific response**

The schematic illustration of Figure 2 represents the situation that prevails in an NP detection mode. For this mode, H$_2$ and air gases are supplied to the detector, and a thermionic source of moderate work function (i.e., TID-2) is operated hot enough (600$^\circ$ to 800$^\circ$C) to cause thermal/chemical decomposition of the H$_2$ and O$_2$ gases. A critical parameter in this NP mode is the restriction of the H$_2$ to low flows (e.g., 3 to 6 ml/min) which are not sufficient to maintain a self-sustaining flame at the sample conduit (i.e., jet structure) depicted in Figure 2. Instead, a flame-like gaseous boundary layer is created in the immediate vicinility of the hot thermionic source. Since this boundary layer is very reactive chemically, sample compounds are decomposed by the active gas phase chemistry, and electronegative products of decomposition are selectively ionized by surface ionization on the thermionic source. N or P compounds are ionized with especially high specificity by this process. An essential condition for the onset of NP detection is that the thermionic source must be hot enough to “ignite” the boundary layer chemistry. Under these conditions, a thermionic source of moderate work function provides the optimum compromise of sample response signal vs. detector background signal. A low work function ther-
ionization processes identical to those which occur in a conventional FID, and surface ionization processes at the catalytic source structure which especially enhance the ionization efficiency of many heteroatom compounds (especially halogenated and phosphorus compounds).

Like a conventional FID, the magnitude of the gas phase ionization is determined primarily by the magnitudes of $H_2$ and air flows and the size of the jet orifice, so that additional electrical heating of the CFID source has little effect on the gas phase ionization. However, the magnitudes of ionization produced by surface processes at the CFID source are strongly dependent on the electrical heating of the source. Hence, in many cases, response factors for heteroatom compounds can be enhanced to be comparable to hydrocarbons by a judicious selection of source heating current. For this CFID mode of detection, the thermonic/catalytic source of highest work function is most suitable because the flame heat would otherwise cause an excessive thermonic emission background signal. The CFID provides detectivities in the 10- to 100-pg range for most organic compounds.

**FTID: Nitrogen/halogen specific response**

Figure 4 depicts a further detection mode in which the thermionic source and collector electrode structure are positioned well downstream of the active region of a self-sustaining flame. The basic concept (6) of this flame thermionic ionization detection (FTID) mode is to burn sample compounds in a self-sustaining $H_2$/air flame at a flame jet, and to selectively re-ionize electronegative combustion products by means of the thermionic ionization components located downstream. In the FTID, a large physical separation between the flame and the thermionic source/collector electrode provides minimal collection of ionization produced in the flame, but excellent collection of ionization produced at the heated surface of the thermionic source. An auxiliary ion-suppress voltage can be applied to further prevent ionization produced in the flame from reaching the ionization collector. This mode of detection provides specific responses to compounds containing N or halogen atoms with a specificity of $10^7$ and detectivity of 1.0 ng. The precombustion of samples in the flame minimizes interferences from sample matrices and provides more uniform responses independent of the original molecular structure of the sample compound. Both the low work function (TID-1) and moderate work function (TID-2) thermionic sources have been used in this FTID configuration. FTID-1 provides good responses to both nitrogen and halogen compounds, whereas FTID-2 responds best for halogen compounds with suppressed nitrogen response.

**Remote FID: Organo-lead specific response**

This mode of detection is a simple variation of the FTID in which no electrical heating is supplied to the thermionic source, and the ion-suppress voltage depicted in Figure 4 is not applied. In this case, the thermionic source serves merely as a polarizer to drive negative ions in the flame effluent to the TID collector electrode. The ionization sensed in this mode corresponds to long-lived negative ions originally produced in the flame. Because of the large separation between the flame and the TID collector electrode, the bulk of the hydrocarbon ionization produced by the flame is dissipated (i.e., positive-negative ion recombination or neutralization at a wall surface) before reaching the TID collector. However, certain heteroatom compounds appear to combust to negative ion products which are especially stable and long-lived. The outstanding demonstration
of this effect is the specific detection of lead compounds in gasoline. Since the thermionic source is not electrically-heated and is not used as a source of surface ionization, any type of thermionic source may be employed in this mode.

Experimental

The applications data presented in this report were obtained with equipment previously described (5,6,14). All the data were obtained using a Model 3740 gas chromatograph (Varian Associates) equipped with either a TID/CFID detector assembly (TID-1-N₂, TID-1-air, TID-2-H₂/air, and CFID modes) or an FTID/TID detector assembly (FTID and remote FID modes) (Detector Engineering and Technology). The TID-1, TID-2, and CFID thermionic emission sources were also manufactured by Detector Engineering and Technology, as was the Model 4000 detector current supply. Negative ionization signals from the detector were measured using the differential electrometer (Varian) in a negative polarity configuration.

The detector assemblies mounted onto the FID-base on the GC, so that different detector gas environments were implemented by plumbing in the appropriate gas through the two gas lines that normally supply 
H₂
and air to an FID. Typical gas flows supplied for different modes of detection are detailed in Table II.

All the data presented in this report were obtained using glass columns, 6 ft x \( \frac{1}{4} \) in. x 2 mm i.d., packed with either 3% SP-2250, 3% SP-2100, or 1% SP-1240 DA on 100/120 Supelcoport (Supelco) or 80/100 Chromosorb 102. The GC carrier gas in all cases was N₂ at a flow rate of 30 ml/min. For complex samples like gasoline, the chromatographic separation was intentionally very poor in order to produce a challenging detector environment to demonstrate specificity of response in the simultaneous presence of many overlapping compounds.

Sample mixtures that were analyzed included a TSD test sample (ng levels of azobenzene, methyl parathion, and malathion) (Varian); Base-Neutral 1 sample (Supelco); phenol mix (Supelco); DCMA PCB mixture (Supelco); and nitroaromatic mixture (Supelco) diluted in reagent-grade benzene. Gasoline, cologne, and diesel fuel samples were analyzed by direct injection of 0.5 to 1.0 \( \mu \)l amounts onto the column. Other samples chromatographed were 1% v/v each mixture of acetone and carbon tetrachloride in water; and an 11% v/v each mixture of methylene chloride, n-C₆, benzene, i-C₆, toluene, n-C₇, p-Xylene, n-C₈, and n-C₉.

Table II. Typical Gas Flows Supplied for Each Mode of Detection

<table>
<thead>
<tr>
<th>Mode</th>
<th>Gas 1</th>
<th>Gas 2</th>
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<tbody>
<tr>
<td>TID-1-N₂</td>
<td>10 ml/min N₂</td>
<td>60 ml/min N₂</td>
</tr>
<tr>
<td>TID-1-air</td>
<td>10 ml/min air</td>
<td>60 ml/min air</td>
</tr>
<tr>
<td>TID-2-H₂/air</td>
<td>3 ml/min H₂</td>
<td>60 ml/min air</td>
</tr>
<tr>
<td>CFID</td>
<td>25 ml/min H₂</td>
<td>200 ml/min air</td>
</tr>
<tr>
<td>FTID</td>
<td>20 ml/min H₂</td>
<td>200 ml/min air</td>
</tr>
<tr>
<td>Remote FID</td>
<td>20 ml/min H₂</td>
<td>200 ml/min air</td>
</tr>
</tbody>
</table>

Applications

Specially formulated test samples are often employed to demonstrate the specificity and sensitivity of NP detectors. The data in Figure 5 correspond to such a test sample comprised of 2.2 ng each of azobenzene (AZO) and methyl parathion (MP), 4.4 ng of malathion (P), and 4400 ng of n-C₁₁ in a solvent of iso-octane. The data illustrate clearly the substantial differences in response between two different modes of thermionic detection, and the very high specificity of the TID-1-N₂ mode for sensing the NO₃ group in methyl parathion. The ionization signals in both chromatograms are very large, indicating detectivities in the pg and sub-pg range.

Figure 6 shows another comparison of the TID-1-N₂ mode vs. the NP mode of detection for a sample consisting of 15 pg amounts of the 2,4- and 2,6-isomers of dinitrotoluene in a relatively impure, reagent grade benzene solvent. For many nitro-compounds, the TID-1-N₂ mode provides substantial improvements in specificity and sensitivity in comparison to an NP mode. However, the NP mode (i.e., TID-2-H₂/air) provides more universal detection for all N-compounds. In Figure 6, the differing magnitudes of TID-1-N₂ signals for the two dinitrotoluene isomers also demonstrate that the TID-1-N₂ signals are very sensitive to the detailed electronegative character of the sample’s molecular structure.

Figure 7 shows the differing responses of six modes of thermionic detection in the analysis of base neutral compounds of concern as water pollutants. The CFID provides universal response to all compounds in this sample with a relatively uniform sensitivity of 0.01 coul/gC. The TID-1-N₂ mode of opera-

*Data presented are from References 6 and 14.

Figure 5. Chromatograms showing two modes of response to a test sample containing a large concentration of a hydrocarbon (C) and trace levels of azobenzene (AZO), methyl parathion (MP), and malathion (MAL). Both chromatograms were recorded at the same sensitivity of 128 x 10⁻¹¹ amps/mV. Column: SP-2250, isothermal at 210°C.
tion provides very specific responses only to a nitro-compound (2,6-dinitrotoluene) and a chlorinated compound (3,3'-dichlorobenzidine). The lack of significant TID-1-N₂ response to nitrobenzene, bis[2-chloroethyl]ether, bis(2-chloroisopropyl)ether, or 4-bromophenyl-phenyl-ether demonstrates that the TID-1-N₂ response depends on how the electronegative functionalities are bound up in the molecular structure of the sample compound. When the detector gas environment of the TID-1 source is changed from N₂ to O₂, the TID-1-O₂ mode provides enhanced relative responses to the chlorinated compounds and a diminished relative response to the nitro-compound. The TID-1-O₂ mode continues to provide good discrimination in favor of chlorinated compounds with respect to hydrocarbons, while exhibiting some low level responses to phthalate compounds. The TID-2-H₂/air mode responds to all the N-compounds, with some small interferences from chlorinated compounds. The FTID-1 mode uses a TID-1 source and provides responses to all the nitrogen and halogen compounds in the sample. The FTID-2 mode uses a TID-2 source which produces responses to the halogenated compounds but suppressed responses to nitrogen compounds in comparison to FTID-1. This set of six chromatograms provides a good illustration of how the detector response can be varied through simple changes in the composition of the detector gas environment.

Figure 8 shows chromatograms of a sample mixture consisting of 75 ng each of 2-chlorophenol, 2-nitrophenol, phenol, 2,4-dimethylphenol, and 2,4-dichlorophenol; 225 ng each of 2,4,6-trichlorophenol, and 2,4-dinitrophenol; and 375 ng each of 4-chloro-m-cresol, 4,6-dinitro-o-cresol, pentachlorophenol, and 4-nitrophenol. The CFID provides a relatively uniform response of 0.004 coul/g·C for all these compounds. (Note: The flame tip orifice for these CFID data was 0.062 in. instead of 0.031 in., which is normally used. The smaller orifice usually provides improved sensitivities of approximately 0.01 coul/g·C.)

The CFID data provide a good illustration of a principal difference in the responses of a CFID vs. a conventional FID. It is well known that conventional FIDs provide relatively uniform response to many hydrocarbon compounds. However, when heteroatoms, such as O, Cl, or P, are present in the sample compounds, the FID response is frequently significantly lower than its response to hydrocarbons. In contrast, the CFID appears to yield more uniform response to all organic compounds in-

Figure 7. Chromatograms showing six different modes of detector response to a sample of base neutral compounds. In increasing order of retention time, the components of the sample are bis(2-chloroethyl)ether; bis(2-chloroisopropyl)ether; nitrobenzene;acenaphthylene; dimethylphthalate; 2,6-dinitrotoluene; 4-bromophenyl-phenyl ether; di-n-butylphthalate; bis(2-ethylhexyl)phthalate; 3,3'-dichlorobenzidine; and benz(α)fluoranthene. Column: SP-2250; 100°C, held for 4 min, then 100°C to 270°C at 15°C/min.

Figure 6. Chromatograms comparing the responses of the TID-1-N₂ mode and the TID-2-H₂/air (NP) mode to traces of dinitrotoluenes. Column: SP-2100, 160°C to 200°C at 10°C/min.
respective of whether they are hydrocarbon or heteroatom compounds. This is the result of the additional ionization process that occurs at the surface of the catalytic CFID source.

As anticipated, the TID-1-N₂ mode in Figure 8 provides high specificity and sensitivity to certain nitro- and polychlorinated-phenols. The responses to pentachlorophenol and 4-nitrophenol are more than 100 times larger than the CFID responses to these compounds. Comparing the responses of 4-nitrophenol and 2-nitrophenol again illustrates a significantly greater TID-1-N₂ response for the isomer with the nitro group located at the 4-position in the molecule.

In the third chromatogram in Figure 8, the low work function thermionic source (TID-1) was operated in a detector gas environment comprised of approximately equal flows of N₂ and air. This illustrates that the composition of the gas environment is an additional parameter which can be used to suppress the response to certain compounds while enhancing the response to others.

The bottom chromatogram in Figure 8 shows the analysis of the phenol sample for the case where both detector gases 1 and 2 are air. Responses are now obtained for all the chlorinated and nitro-phenols, with the dinitro-compounds continuing to give the dominant responses. The responses to 2-nitrophenol and 4-nitrophenol are now comparable, in contrast to the TID-1-N₂ response in which there was significant preference for the nitro group in the 4-location vs. the 2-location.

Figure 9 demonstrates the high specificity for lead alkyls in

![Figure 8. Chromatograms showing different modes of detector response to phenol sample containing 2-chlorophenol; 2-nitrophenol; phenol; 2,4-dimethylphenol; 2,4-dichlorophenol; 2,4,6-trichlorophenol; 4-chloro-m-cresol; 2,4-dinitrophenol; 4,6-dinitro-o-cresol; pentachlorophenol; and 4-nitrophenol in order of increasing retention time. Column: SP-1240, 100° to 210°C at 8°F/min.](image)

![Figure 9. Chromatograms illustrating the specific detection of lead alkyls in gasoline using the remote FID. Data correspond to samples randomly obtained from local gasoline stations. Column: SP-2100, 50° to 230°C at 15°F/min.](image)
gasoline provided by the remote FID mode of detection. Previously, GC/atomic absorption spectroscopy (AAS) instrumentation has been described for the specific detection of lead alkyls in gasoline or other samples (15). By comparison with AAS, the remote FID provides excellent sensitivity and specificity, and is considerably simpler and less expensive to operate. The data shown in Figure 9 were obtained by direct injections of 0.8-μl amounts of the gasolines onto a temperature-programmed, packed column.

The remote FID mode of detection has some configuration similarities to a hydrogen atmosphere flame ionization detector (HAFID), which has also been reported to provide specific detection of lead alkyls in gasoline (16). Both the remote FID and HAFID use a collector electrode well removed from the flame jet structure. However, the signals in the remote FID are largest with an oxygen-rich flame, whereas the HAFID requires a hydrogen-rich atmosphere doped with silane.

Gasoline is a readily available, complex mixture of organic compounds which is especially well suited to demonstrating the different responses obtained in the family of thermionic detection modes. Figure 10 shows multiple modes of analysis of a sample of regular gasoline. The chromatographic separation was performed on a packed column to purposely create the demanding situation in which many overlapping compounds are present in the detector volume at the same time. This situation is shown to be the case by the CFID response. When the same gasoline sample is chromatographed using the remote FID mode, selective responses are obtained only for the five lead alkyls. The remote FID data in Figure 10 were obtained with an FTID detector assembly and a TID-2 source mounted on a Model 3700 GC (Varian). The detector conditions were $H_2 = 30$, air = 200 ml/min; zero heating current to the TID-2 source; and flame ion-suppress voltage disconnected. The FTID-2 data in Figure 10 correspond to the following changed detector conditions: $H_2 = 30$, air = 80 ml/min; source heating current = 3.2 A; and ion-suppress voltage on. This change in conditions produced an FTID-2 response which was selective for the halogenated lead scavengers, ethylene dichloride (EDC) and ethylene dibromide (EDB). Figure 10 shows that selective responses to EDB and tetraethyllead (TEL) are also obtained in the TID-1-air mode, while the TID-1-N mode provides responses to all the lead alkyls and lead scavengers. Note the large TID-1-N response to TEL in comparison to tetramethyllead (TML), thereby illustrating a greater electronegative character for the TEL molecular structure vs. TML. Note also that precombustion of all samples in the flame of the remote FID mode provides a more uniform response for all lead alkyls irrespective of their original molecular structures.

Figure 11 illustrates six different detector responses in the analysis of diesel fuel containing a trace nitro-compound additive. It is clear from the CFID chromatogram that there are many unresolved component peaks in this packed column analysis. A primary objective of this particular set of analyses was to define the best method of measuring the amount of the nitro-compound added to such samples. The TID-1-N mode clearly gives the best specificity and excellent sensitivity to the nitro-additive. The other specific modes of detection illustrate selective enhancement of other segments of this complex sample in addition to the nitro-additive. For example, the cluster of peaks at late retention times in the TID-2-H$_2$/air chromatogram undoubtedly corresponds to other N-compounds in the sample. The two FTID-1 chromatograms illustrate that the H$_2$/air mixture ratio is a further means of significantly altering the FTID re-

![Figure 10. Chromatograms showing multiple modes of detector response to a sample of regular leaded gasoline. Column and program same as in Figure 9.](image-url)
response. The mixture of 20 ml/min H₂, 100 ml/min air represents an oxygen-rich flame, while the mixture of 35 ml/min H₂, 70 ml/min air is a hydrogen-rich flame. Generally, stoichiometric or oxygen-rich flames are the most useful for the FTID.

Figure 12 shows multiple mode analyses of a commercial brand of cologne. These sets of chromatograms illustrate the advantageous use of the specific detection modes to enhance responses for trace fragrance components in colognes. The TID-I-N₂ mode is especially useful because it is non-destructive. Therefore, TID-I-N₂ emits exhaust gases that are characterized by distinctly different fragrances that change with time as the various segments of the chromatogram elute. For the cologne shown, as well as for other brands that have been examined, the set of chromatograms obtained from the different modes of thermionic detection provide a characteristic fingerprint that distinguishes one brand from another.

All the modes of detection described in this article measure negative ionization currents. The magnitudes of these currents are very dependent on the electronegative character of the chemical species adjacent to the heated thermionic source.

Figure 11. Chromatograms showing different detector responses to a sample of diesel fuel containing a trace nitro-compound additive identified by the asterisk. Column SP-2100, 90° to 270°C at 10°C/min.

Figure 12. Chromatograms showing multiple modes of detector response to a brand of cologne randomly obtained. Column: SP-2100, 100° to 270°C at 10°C/min.
Figure 13 illustrates how the response to a group of polychlorinated biphenyl (PCB) compounds changes with precombustion of the compounds. The data obtained with a TID-2 source in an air environment exhibit large differences in response between the different PCB compounds, similar to the known characteristics of an ECD. The FTID-2 data show that the precombustion of the PCBs yields negative ionization currents, which are larger in magnitude as well as more uniform per Cl atom. In this case of PCBs, precombustion improves the detectability by producing chemical species more electronegative than the original compounds. For other compound types, precombustion sometimes causes the opposite effect of producing combustion products which are not as electronegative as the original compound.

The data in Figure 14 provide an illustration of the relative electronegativity of phenol compounds before (TID-1-air) and after (FTID-1) combustion. The FTID-1 mode of operation can be easily converted to the TID-1-air mode by simply turning off the H\textsubscript{2} fuel to the FTID flame. Figure 14 shows that the FTID-1 mode produces a much more uniform response for all the chloro- and nitrophenols of this sample, but the absolute magnitudes of FTID response for the dinitrophenols, pentachlorophenol, and 4-nitrophenol are substantially lower than the TID-1-air response to these compounds.

Figure 15 illustrates the use of the TID-1-air mode to detect EDB in food products. A simple headspace technique was used for the data. One of the advantages of the TID-1-air mode is that it is insensitive to the large air component in the injection headspace vapors. Hence, all chromatographic peaks that are obtained may be attributed to vapors emanating from the food product itself. In addition to EDB, this sample mixture provided other large TID-1-air signals, thereby suggesting the presence of other halogenated or electronegative constituents that may be of interest in such products. With a better optimization of GC column for the EDB separation, this simple technique should be capable of EDB detection in the 1 to 10 ppb range of concentration in the food product.

Figure 16 illustrates that one difference between a CFID and an FID is that the CFID will provide significant responses to halogenated compounds. Figure 17 further shows that the CFID...
response to halogenated compounds can be selectively enhanced by increasing the source heating current, while the CFID responses to hydrocarbons remain unchanged. Consequently, by judiciously adjusting the source heating current, the CFID response to halogenated and some other heterotatom compounds can be tuned to yield about the same response factor as obtained for hydrocarbons.

Summary

The preceding data have demonstrated that thermionic ionization techniques and equipment have applications in gas chromatography that go well beyond the usual NP detection, such as that of TID-2-H2/air. To achieve the best possible signal-to-noise ratio and specificity for each mode of detection, the specific chemical composition of the thermionic emission source needs to be matched with the temperature and gas phase environment in which the source is operated.

From their extensive use in NP detection, thermionic ionization detectors are known to often exhibit decreasing sensitivity with increasing operating time as a result of depletion of the thermionic source activity. Consequently, the thermionic source usually needs to be replaced at periodic intervals. Of the different modes of detection described in this report, the NP mode is the most demanding with regard to the operating life of the thermionic source. Generally, in modes of detection (e.g., TID-1-N2) where the operating temperature is lower and the gas environment is less reactive, the thermionic sources maintain their responses over longer periods of time. For all modes of detection, a practical guideline for achieving the longest possible source lifetime is to operate the thermionic source just hot enough to achieve the response required.

The developments of thermionic techniques in GC have also spawned applications of the technology in liquid chromatography detection (17), thin layer chromatography (18), and mass spectrometry ion sources (19). Since there remain to be studied many different combinations of thermionic source compositions, thermionic source temperatures, and gas environment compositions, it is probable that the technology will continue to evolve in coming years.

Figure 16. Comparison of CFID and FID responses to a water sample containing acetone and carbon tetrachloride. Column: Chromosorb 102, isothermal 120°C.

Figure 15. Example of TID-1-air application to determine EDB in cake mix. Sample: headspace vapors from 0.7 gm Duncan Hines Deluxe Yellow Cake Mix in a sealed 2-ml vial. Sampling procedure: heat sealed sample vial to 120°C; extract 200 μl headspace vapor with gas-tight syringe; inject into GC and start column oven temperature program. Column: SP-2100, 40°C to 110°C at 10°C/min.

Figure 17. Comparison of CFID responses to sample of methylene chloride and various hydrocarbons at two different magnitudes of heating current to the catalytic source. Column: SP-2100, 40°C to 180°C at 10°C/min.
References


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