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ABSTRACT

MEASUREMENT OF OXYGENATED VOLATILE ORGANIC COMPOUNDS USING THE THERMIONIC IONIZATION DETECTOR

by
Wanfang Li

A thermionic ionization detector (TID) consists of a catalytically active, low work function heated source. It responds to molecules with high electron affinity which can extract electrons from the surface of the source to form negative ions. TID has been used as selective detectors for nitrogen and phosphorous compounds (NPD). In this research, a TID has been used for selective detection of oxygenated volatile organic compounds (VOCs). The response of the TID to different oxygenated and chlorinated VOCs compounds was studied. To evaluate its performance, the analysis was done using a FID in parallel with the TID. For most of the compounds studied, the TID exhibited selective responses in presence of hydrocarbons with reasonable sensitivity and linearity. Effects of various TID operating parameters, namely detector temperature, source current supply and bias voltage were studied.

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USING THE THERMIONIC IONIZATION DETECTOR**

by
Wanfang Li

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APPROVAL PAGE

MEASUREMENT OF
OXYGENATED VOLATILE ORGANIC COMPOUNDS
USING THE THERMIONIC IONIZATION DETECTOR

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This thesis is dedicated to my dear husband

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CHAPTER 1

INTRODUCTION AND BACKGROUND

The analysis of volatile organic compounds (VOCs) in air is particularly challenging because they are usually present in very low concentration (ppm_v to ppb_v level). VOCs in emission sources and ambient air are analyzed either using whole air samplers such as tedlar bags and canisters (e.g., EPA Method TO14) or using sorbent cartridges (e.g. EPA Method TO1, VOST). The analysis is usually done using a GC with flame ionization detector (FID) or a mass spectrometer (GC/MS). Selective detectors are available for halogenated compounds (e.g., ECD, ELCD), for sulfur compounds (e.g., FPD) and nitrogen containing compounds (e.g., NPD).

Oxygenated VOCs such as alcohols, aldehydes and ketones are an important class of pollutants, especially with the introduction of oxygenated compounds in gasoline. Because of the high toxicity of organic bound lead, elimination of lead - containing compounds in gasoline is necessary. The components frequently used as fuel additives in unleaded gasoline are oxygenated substances such as methanol, ethanol, butanol and methyl t-butyl ether (MTBE). According to new regulation, the organic-bound oxygen in gasoline must be at least of 2.7% [1, 2]. Thus, the automobile exhaust contains relatively large amounts of oxygenated VOCs as well. As the use of these oxygenated compounds becomes more widespread. It will become necessary to establish a suitable analytical method for the detection of these compounds.

Since auto exhaust contains hundreds of aliphatic and aromatic hydrocarbons, it is analytically difficult to detect the different oxygenated VOCs without interference. A few gas and liquid chromatographic methods have been used to detect the oxygenates in the gasoline [3-7]. These methods generally require a complex column switching or extraction procedures to separate the oxygenates from hydrocarbons. Luke and Ray [3] employed a

column switching technique to quantitate common alcohols and MTBE levels in gasoline. Aqueous extraction of the gasoline had to be done before the gas chromatographic analysis [4]. Unfortunately, these methods are very cumbersome. The analysis is significantly simplified if a selective GC detector is employed, because then there is less demand on the chromatographic separation.

The most commonly used detector for VOCs analysis is the FID, which is not very sensitive to most of the oxygenated compounds, and it would be of great advantage to have a detector that can selectively identify the oxygenated VOCs in a complex matrix containing different aliphatic and aromatic hydrocarbons. However, the detector should show no response to oxygen containing gases present in the atmosphere, such as CO, CO₂, H₂O, etc. There are two types of specific detectors currently available for selective detection of oxygenated compounds: O-FID (Oxygen-Sensitive Flame Ionization Detector, marketed by ES industries and Siemens Chromatographs, Berlin, New Jersey); and AED (Atomic Emission Detector, marketed by Hewelett Packard).

A schematic diagram of O-FID is shown in Figure 1 (Appendix A). The detection system contains three main parts: a thermal cracker reactor, a methanizer and a regular FID. The cracker reactor consists of a tube made of catalytic material which is heated to about 1200°C. When the sample from the column gets inside the cracker tube, all hydrocarbon molecules are completely decomposed into their elements such as carbon, hydrogen, etc.. When oxygenated compounds are present, the oxygen is produced as a decomposition product. Hydrogen is flushed together with the carrier gas and passes undetected through the detector. Each oxygen atom forms a carbon monoxide molecule with one carbon which is predeposited on the cracker. The carbon monoxide reaching the methanizer is converted to methane in the presence of hydrogen. The methane is then detected with a conventional FID [8-10]. The O-FID detection system responds only to oxygen containing compounds and ignores the presence of compounds without oxygen. Therefore, it is a selective detector for oxygenates, and has been used in the analysis of

oxygenates in gasoline. However, O-FID does not provide any structural information except that the compounds containing oxygen. And because O-FID responds only to the oxygen in the compound, this detector's response is proportional to the percent oxygen in the compound. The O-FID response decreases with increase in molecular weight of the oxygenates[10, 11].

Atomic Emission Detector measures the emission released by an atom's electrons after it is excited to a higher energy level in a plasma source (usually a microwave induced plasma). As shown in Figure 2 (Appendix A), in GC-AED, the detector contains a helium discharge chamber, powered by a microwave generator. Here the sample molecules are disintegrated into atoms which are thermally excited in the plasma. When the electron goes from higher energy level back to the ground state the excess energy is radiated as photons of specific wavelength. The emitted radiations are dispersed by a diffraction grating and the intensity at different wavelength is measured using suitable detectors. Oxygen specific detection is achieved by measuring the intensity of the wavelength corresponding to the oxygen emission. The AED is expensive, and so far its practical application is limited to laboratory research [12-14].

Both O-FID and AED function by completely decomposing the incoming sample. Their responses depend on the elemental oxygen irrespective of its source [2]. Therefore, they respond to the oxygen containing gases O_2 , CO, CO_2 and H_2O , etc.. These gases are always associated with air samples, and their presence makes air analysis with either O-FID or AED difficult. Even a small air leak can significantly increase the background noise and result in the reduction of sensitivity.

In this research we explored the possibility of using a Thermionic Ionization Detector (TID) for oxygen specific detection. The use of thermionic ionization detector for GC dates back to the 1970's when the modern TID was first introduced by Kolb and Bischoff [15] to measure nitrogen and phosphorus compounds (NPD). Most studies and applications of the TID so far have focused on the analysis of nitrogen, phosphorus

compounds [16-26], and halogenated compounds [25, 27]. Unfortunately, a systematic analytical method for oxygenated compounds using the TID is not available.

A schematic diagram of the Thermionic Ionization Detector (TID) is shown in Figure 3 (Appendix A). The TID consists of a low work function, catalytically active thermionic source which is cylindrical in shape and is located in the axis of a cylindrical collector electrode. It is electrically heated by an electric current to a temperature of 400° C to 600°C in a gaseous environment. This catalytically active source is biased at a negative potential with respect to the collector electrode. The thermionic surface of the source is composed of a ceramic material containing a high concentration of alkali metals which has a relatively low work function which is defined as the amount of the energy required to remove an electron from the gaseous atom at lowest energetic state [31]. The detector is generally positioned onto an FID-type detector base so that two sources of detector gases can be supplied. The TID functions by a process involving the extraction of electrons from the surface of the electrically heated source. The sample molecules carried out of the GC column are mixed with one of the detector gases and enter the detector through the sample conduit tubing. When the molecules strike the heated, alkali-activated ceramic surface of the source, the sample molecules are ionized to form a gas phase negative ion flow by extraction of an electron from the surface. Negative ionization current is measured with a standard electrometer [28-30].

The most important component of the TID is the thermionic source, whose characteristics depend upon factors such as: the surface composition of the source, the temperature of the source, and the composition of the gases around the source. Alkali metal compounds are added to the ceramic matrix to lower the work function so that electron emission from the thermionic surface becomes easier. The work function of the thermionic source depends on both the type of the alkali metal and the percentage of alkali used in the source composition. The work function (or ionization energy) of the alkali metals are in decreasing order: Na > K > Rb > Cs. For two sources composed of different

percentages of the same alkali metal compound, the source with the higher percentage of alkali metal has the lower work function and more easily allows the thermionic emission of charged particles from the source.

The work function of the alkali metal on the surface decreases as the source temperature increases. Thus, the sample molecule ionization takes place more readily and higher detector response is obtained at higher temperature. The source temperature is the consequence of a balance between the electrical current input to the source and heat losses due to conduction and convection through the gases flowing past the source. Therefore, the source temperature depends upon the electrical heating current, the detector block temperature, and the thermal conductivity of the gas mixture flowing past the source, and the total gas flow through the detector. The principle function of the detector gases in TID is to maintain a well purged detector volume. The TID is a mass flow rate sensitive detector rather than a concentration sensitive detector. The relatively high flows of detector gases are used to sweep the detector volume without causing reduced responses due to sample dilution effect. However, the composition and the flow rate of detector gases do affect the temperature of the source surface. Generally, the flow rates of gas 1 and gas 2 are 10-15 ml/min and 60-80 ml/min, respectively.

CHAPTER 2

RESEARCH OBJECTIVE

The objective of this research was to evaluate the use of thermionic ionization detector for selective detection of oxygenated VOCs. The effect of various parameters on sensitivity and selectivity of the TID for oxygen specific detection was studied. A TID and a FID were used in parallel for comparison purpose. The idea was that the FID would respond to all VOCs and the TID would respond only to oxygenated and chlorinated compounds in air.

CHAPTER 3

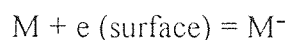
THEORY

As described in chapter 1, the TID function depends upon the surface mechanism such that sample molecules extract electrons from a thermionic source. Thus, the detector responds to compounds containing electronegative functional groups which are capable of capturing electrons to form negative ions. According to the different types of compounds to be detected, three levels of TID response have been classified [29]. The TID has extremely large response to certain compounds containing nitro (NO_2) functional group or polychlorinated compounds. Its detection level is in the range of femtogram and picogram (10^{-15} - 10^{-12} g) - Primary level of response. The TID has relatively lower response to oxygenated compounds such as alcohols, ketones, etc.. The detectivity is in the range of nanogram (10^{-9} g) - Tertiary level. The detection level ranges between the primary level and tertiary level is for chlorinated compounds in the picogram to nanogram (10^{-12} - 10^{-9}) - Secondary level of response. Although the TID responds to oxygenated compounds only at tertiary level, the response is still several orders of magnitude larger than that for the non-electronegative functional groups such as aliphatic hydrocarbons and aromatic hydrocarbons. It is one of the important characteristics of the TID that it has a relatively negligible response to aliphatic hydrocarbon and aromatic hydrocarbon.

The mechanisms of the TID are not completely understood. In previous publications, the mechanism of the NPD response to nitrogen and phosphorus containing compounds have been reported [20, 21, 32]. Before Daniel D. Bombick's work on the response mechanism of the GC/TID, two possible reaction zones were proposed, one in the gas phase and the other on the surface of the source. The result of Bombick's study using mass spectrometry indicated that a reactive gas phase zone seems impossible, and all the steps leading to the formation of ionic species may occur only on the surface of the

alkali-ceramic source [32]. In general, three different mechanisms have been proposed [23] and all of them agree that molecular ions or its derivatives form a negative ion by extracting an electron from the heated, thermionic source.

One possibility is that the sample molecule directly forms a negative ions by extracting electrons from the thermionic source:



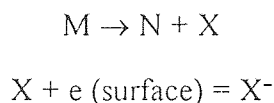
The electron transfer process occurs only between to the sample molecule and the surface. Therefore, the concentration of molecular negative ion is calculated as below:

$$[M^{-}] = k [M] [e]$$

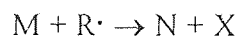
Where, k is an constant; $[M]$ and $[M^{-}]$ are the concentrations of sample molecule and molecule ion respectively; and $[e]$ is the concentration of electron of the surface. The electron concentration depends upon surface composition of the source and TID operating conditions such as detector current, surface temperature, and bias voltage. For a given source, k depends upon the structure of the analyte. A correlation between k and electron affinity has been suggested [33], the higher the electron affinity, the easier it is to extract an electron from the surface. So, the larger the constant k , the higher is the sensitivity of the TID for that molecule. Since halogenated and nitro-compounds have relatively high electron affinities, the TID is extremely sensitive to these compounds. The oxygenated compounds, in general, have lower electron affinity; thus, the TID is less sensitive to these compounds, yet more sensitive than to the hydrocarbons.

It has been suggested that the sample molecule itself may not become negatively changed directly. Instead, the molecule is thermally decomposed on the hot surface and

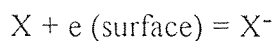
one of the fragments with a high electron affinity forms a negative ion by abstracting the electron from the surface:



Alternatively, the sample molecule interacts with a gas phase radical $R\cdot$ and decomposes on the hot surface:

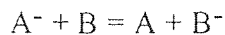


The decomposition product X then abstracts an electron from the surface to form its negative ion X^- :



Associative electron attachment is another possible mechanism where two or more sample molecules, or their dissociated fragments interact with each other while resident on the thermionic surface. The associative electron attachment process usually is not expected, but may occur only when the concentration of the sample is very high and is characterized by the non-linearity of the signal response with increasing sample concentration.

The formation of negative ion of the sample molecule (M^-) or the negative ion from one of the decomposition products (X^-) depends upon their ability to extract the electron from the thermionic surface. Electron affinity (EA) which is defined as the ability to obtain electrons to form negative ions seems to be a suitable parameter to describe the ability to abstract electrons. For example, an ion-molecule equilibrium such as:



The equilibrium constant K can be calculated from the electron affinity of species A and B as follows:

$$K = [B^-][A]/[A^-][B]$$

$$-\Delta G^\circ = -RT \ln K$$

$$-\Delta G^\circ = -\Delta H^\circ - T(-\Delta S^\circ)$$

For $-\Delta S^\circ$ is very small that it may be neglected,

$$-\Delta G^\circ \cong -\Delta H^\circ = EA_A - EA_B$$

$$K = \exp(-\Delta G^\circ/RT) = \exp\{-[EA_A - EA_B]/RT\}$$

Here, [A], [B], [A⁻] and [B⁻] are the concentrations of species A, B and their corresponding negative ions. In the thermodynamic reaction, ΔG° is the change of standard Gibbs free energy, ΔH° is the change of standard enthalpy, ΔS° is for the change of standard entropy. R is gas constant and T, absolute temperature. EA_A and EA_B are the electron affinity of species A and B respectively [35].

When the electron affinities of A and B are available, the equilibrium constant K can be measured as above. Molecules with higher electron affinity are expected to have a bigger equilibrium constant K; thus, higher response in the TID. Unfortunately, little electron affinity data is available for oxygenated compounds, a situation which hinders the further research on the TID mechanism.

CHAPTER 4

EXPERIMENTAL

4.1 Reagents

Most of the work presented here was done with a standard gas mixture prepared by Alphagaz Inc. (Morrisville, PA). The liquid standard sample was mixed from chromatography grade chemicals. The gasoline analyzed was produced by Exxon.

4.2 Instrument

The diagram for the analytical system is shown in Figure 4 (Appendix B). Stainless steel tubes 6" in length and 1/4" in outer diameter were employed as sorbent cartridges. They were conditioned 24 hours in an oven at a suitable temperature with a 20 ml/min flow rate of N₂ for each tube. Air samples and automobile exhaust samples were collected using a personal sampling vacuum pump (GilAir-5, Tri-Mode Air Sampler, Gilian Instrument Corp., Caldwell, NJ).

A automatic thermal desorber (Model 5010 Automatic Desorber, Tekmar Company, Cincinnati, Ohio) was used for the desorption of VOCs from the sorbent cartridges. The desorption was carried out in a flow of He at the rate of 20 ml/min.

A TID made by Detector Engineering and Technology Inc., (Walnut Creek, CA) was used for analysis. An analysis was performed by two detectors (FID and TID) mounted on a Varian 3400 Gas Chromatograph. Model 1075 split capillary injector was used for direct liquid mixture injection. A 50 meter long crosslinked methylsilicone column (HP PONA) with 0.2 mm i.d. and 0.5 um film thickness was used in the analysis. Column effluent was split into two parts by a SGE 1:1 splitter which fed both the FID and TID.

A Varian Saturn II Gas Chromatograph / Mass Spectrometry was employed to perform the qualitative analysis when necessary. All GC data were collected and processed by Fisons PC-Minichrom chromatography data system.

4.3 Sampling

Most of the work was done with gas standards, and actual samples were also analyzed. The sampling of VOCs in the standard gas mixture, ambient air and automobile exhaust was done using sorbent cartridges which contained multiple beds of adsorbents (e.g., EPA Method TO-1) such as Carbotrap, Carboxen (Supelco Inc.) or Tenax, etc. In order to get a higher trapping efficiency, different adsorbents were tried rather than a single one. The best results were obtained with beds of multiple adsorbents. Figure 5 (Appendix B) shows the cartridge with multiple adsorbents. The silanized glass wool was used to separate the adsorbent beds. From the sampling direction, the least volatile were trapped by the Carbotrap B (7 cm). Intermediate compounds were trapped on Carboxen 1000 (5 cm). Only the most volatile molecules reached the third adsorbent area where they were trapped by Carboxen 1001 (1 cm).

A schematic diagram of the arrangement is shown in Figure 6 (Appendix B). The sample flow rate was controlled by a flow controller (Porter Instrument Company, Hatfield, PA). The Volume of Standard gas sampled by the cartridge was calculated by the graduated cylinder. Since the standard gas was made using nitrogen, which is not adsorbed in the cartridge, the displaced water volume equals the total gas volume passed through the cartridge estimably.

VOCs in gasoline were sampled by collecting the head space vapor of a sample bottle. Sampling was carried out at 1.5 ml/min for 10 seconds. Automobile exhaust was collected directly from an automobile tailpipe at 15 ml/min for 15 minutes. Both types of samplings were done using Gil-Airs pumps. The amount of sampling was easily controlled by adjusting the flow rate and sampling time of the pump.

4.4 Analysis

The samplers were heated in a model 5010 automatic thermal desorber and automatically transferred to the GC, as shown in Figure 7 (Appendix B). Sample trap loading and unloading are easily achieved with the desorber. All flows are positively directed through the trap. The trap is loaded when the heater is cool. A prepurge is carried out before heating, which enables oxygen to be completely displaced from the tube before heating. The presence of oxygen at elevated temperature decreases the lifetime of the sorbent used. After the prepurge, an internal trap is cooled to a preset temperature of about -150°C using liquid nitrogen. Then the tube is heated rapidly and simultaneously swept with helium to desorb the VOCs from the sorbent, which are retrapped in the internal trap. After the completion of the desorption step, a six-port switching valve is rotated to let the GC carrier gas backflush the internal trap, which is rapidly heated. The sample is then swept to the GC by the carrier gas, and analyzed. The operating desorption parameters are shown in Table 1. Table 2 summarizes the operating conditions of the gas chromatograph.

Table 1 Operating Conditions of Automatic Desorber

Purge-1 Time (min)	5.00
Cryo Cool-1 (°C)	-150
Purge-2 time (min)	0
Furnace Desorb (°C)	360
Desorb Time (min)	10.00
Cryo Cool-2 (°C)	-150
Transfer Time (min)	10.00
Cryo-2 Inject (°C)	210
Inject Time (min)	0.75
Furnace Bake (°C)	320
Line Heater (°C)	210
Valve Heater (°C)	270
Injector Heater (°C)	210
Furnace Ready (°C)	40

Table 2 Operating Conditions of Gas Chromatograph

Injector Temperature	210 °C	
Column Conditions	Carrier Gas (He) at 0.77 ml/min	
FID Conditions	Temperature	320 °C
	Attenuation	8
	Range	10
	Hydrogen	31.8 ml/min
	Air	300 ml/min
	Make Up (N ₂)	22.3 ml/min
TID Conditions	Temperature	320 °C
	Attenuation	8
	Range	11
	Gas 1 (N ₂)	13.6 ml/min
	Gas 2 (N ₂)	64.4 ml/min
	Source Current	2.40 to 2.70 amp
	Bias Voltage	45 V

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Characteristics of TID Response

The TID response is selective towards molecules with strong affinity for electrons. Since hydrocarbons have low electron affinity, the TID response to these compounds is very weak. Figures 8 and 9 (Appendix C) are gas chromatograms of two different standard VOCs mixtures containing ppm_v levels of different aliphatic, aromatic hydrocarbon as well as chlorinated, nitrogenated and oxygenated compounds. Figure 10 (Appendix C) is a gas chromatogram of a liquid VOCs mixture containing ng levels of some of the above mentioned compounds. It can be seen that the TID had a strong response to oxygenated, chlorinated and nitrogenated compounds but showed negligible response to aliphatic and aromatic hydrocarbons. Figures 11 and 12 (Appendix C) show gas chromatograms of gasoline and auto exhaust sample, respectively. No attempt was made to identify the different compounds. However, it can be seen that many fewer peaks are seen in the chromatogram of the TID than that in the FID because it responded only to oxygenated (or compounds with high electron affinity) compounds, which confirms that TID is more selective than FID.

The ratio of responses of the TID to that of the FID for different compounds are presented in Table 3.

Table 3 Response Ratio of TID to FID for Some Compounds

Compound	TID/FID	
	#1	#2
Oxygenated		
Methanol	18	22
Ethanol	14	16
1-Propanol	13	11
2-Propanol	8	7
Butanol	8	---
Octanol	4	5
Propionaldehyde	42	---
Acetone	3	---
MEK	11	2.8
MIBK	6	2.2
Acetophenone	5	1.2
Diethyl Ether	0.5	---
Methyl Acetate	4	4
Ethyl Acetate	5	35
Nitrogenated		
Acetonitrile	40	14
N,N-Dimethyl Formamide	2	---
Halogenated		
Epichlorohydrin	70	50
Methyl Chloride	123	---
1,1-Dichloroethane	43	---
1,2-Dichloroethane	32	---
1,1,1-Trichloroethane	30	---
Trichloroethylene	60	---
Chlorobenzene	0.6	---
1,2-Dichlorobenzene	4	---
Chloroform	120	---

Column condition: Hold at 0°C for 1 min, then 4°C/min to 180°C.

Two thermionic sources were evaluated in this research, identified as #1 and #2. The FID is known to be more sensitive towards hydrocarbons than towards oxygenated compounds. It was seen that TID response towards oxygenated compounds like alcohols, aldehydes, ketones, etc. was comparable to that of the FID. With the exception of chlorobenzene, the TID/FID ratio was higher for the chlorinated compounds than for oxygenated ones. The TID/FID ratio did not change significantly with sample concentration and it remained constant during long periods of operation. For the alcohols studied here, the TID/FID ratio decreased as the molecular weight increased.

The TID response is sensitive to the structure of the molecule. For example, the TID showed a lower response to iso-propanol than to n-propanol. To a certain extent, the TID/FID ratio depends upon the functional group, but these values are not unique to each group. For instance, based on the absolute value of the ratio one could not predict whether a certain compound was an alcohol, and aldehyde or ketone. Since the TID/FID ratio is much higher for chlorinated compounds than the oxygenated ones, it may be possible to distinguish between chlorinated and oxygenated compounds.

The detector had no response to CO₂, CO and showed very low response for H₂O. Figure 13a (Appendix C) are chromatogram of liquid samples with and without water. It can be seen that water had practically no response in the TID. Only when large amount of water was injected, TID showed small response as shown in Figure 13b (Appendix C).

The most useful property of TID is its selectivity towards oxygenated compounds and halogenated compounds. The selectivity with respect to the hydrocarbons was calculated as:

$$\text{Selectivity} = S_x / S_{hy} \quad (1)$$

where, S_x and S_{hy} are responses of the TID to oxygenated (or halogenated) compounds and hydrocarbons, respectively. Selectivities of some oxygenated compounds and

halogenated and nitrogenated compounds relative to some hydrocarbons are shown in Table 4.

Table 4 Selectivity of TID for Some Compounds with Respect to Hydrocarbons

Compound					
	MCP	Hexane	Iso-Octane	Octane	Toluene
Methanol	81	326	11	18	244
Ethanol	307	1126	42	69	920
1-Propanol	251	1004	35	59	753
Octanol	22	400	14	22	299
Methyl Acetate	214	857	30	48	643
Ethyl Acetate	251	825	29	46	618
Acetonitrile	1142	456	158	255	3425
1,2-Dichloroethane	2390	9558	331	534	7169
Epichlorohydrin	1517	6068	210	339	4551

MCP: Methylcyclopentane, Source Current- 2.70 amp

Under this particular operating condition, the selectivity varied anywhere from ten to ten thousand. Since S_{hy} varies from compound to compound, so does selectivity. In general the selectivity with respect to the aromatic hydrocarbons was higher than that for aliphatic ones. The structure sensitivity of the TID is again demonstrated by the fact that selectivity with respect to the iso-octane and n-octane were quite different.

The selectivity is a function of the TID source current. Selectivities of some oxygenated compounds with respect to hexane and pentane are presented in Figures 14a and 14b (Appendix C), respectively. When the source current is decreased, the selectivity increases. The increase is exponential in nature. Figures 15a and 15b (Appendix C) show

the exponential relationship between the selectivity and the source current for pentane and hexane. However, when the source current is decreased, the absolute response of the TID also decreases. Figure 16 (Appendix C) shows that as the current increased, the absolute response of the TID increased. So there is a trade off between sensitivity and selectivity when the source current is varied. For example the selectivities presented in Table 4 were obtained at a source current of 2.7 amp. The selectivity is low at this source current, but provides the high sensitivity required in trace analysis.

5.2 Effect of TID Operating Parameters

The TID operation is a function of its operating parameters, namely: detector temperature, source current, and bias voltage between the electrodes. The TID response increased with increased detector temperature. The variation in TID response with detector temperature was studied for some oxygenated and chlorinated compounds in the range of 260°C and 350°C. Effect of detector temperature on TID response to some compounds was shown in Figure 17 (Appendix C). The effect of detector temperature was not very significant because the response increased only marginally. The increase in response is more or less linear up to 330°C, beyond which the response seemed to increase more rapidly. However, it is not possible to capitalize on this higher sensitivity because the suggested operating temperature range is between 260°C to 320°C. Operating at higher temperatures reduces the life of the detector.

As mentioned before, the key component of TID is its thermionic surface containing a high concentration of alkali metal. When the detector source current is increased, the source temperature increase, thus lowering the work function of the alkali metal on the surface so that the ionization takes place more readily, and a higher detector response is obtained. The ionization level in a TID can be varied over a wide range by changing the current supply to the thermionic source. It has been suggested that in a NPD the response increase exponentially with source current [17, 23]:

$$R = k \exp (bI) \quad (2)$$

where, R is the NPD response, I is the source current, k and b are constants. The response of TID towards the oxygenated compounds varied with source current as shown in Figure 18 (Appendix C). The response increased exponentially with the source current as presented Figure 19 (Appendix C). Significant increase in detector response can be obtained by increasing the source current, but this is accompanied by lower selectivity as shown in Figure 15. The selectivity also decreases exponentially with an increase in source current. The source current also seemed to affect peak shape. At low source current, some compounds showed peak tailing.

Another factor that effects the TID response is the bias voltage. When the source is biased to a more negative voltage, the negative ion formation is easier and the detector response increases. The effect of the bias voltage on TID response is shown in Figure 20. The TID response increased with increase in bias voltage. The bias voltage affected the response of some compounds more strongly than others. For example, in Figure 20 (Appendix C) the increase in response with bias voltage was more pronounced for dichloroethane than for methanol. The TID showed a liner response over a wide range of concentrations. Calibration curves for several VOCs including alcohols, ketones, chlorinated and nitrogen containing compounds are presented in Figure 21 (Appendix C). Non-linearity was observed at higher concentrations. This is consistent with a previous study [29], where associative electron attachment to the molecules (or their fragments) at higher concentrations was suggested as the reason for non-linearity.

The detection limit of the TID response also depends upon the source current. It is calculated as [34]:

$$S_m = S_{bl} + kS_{bl}$$

$$S = mC + S_{bl}$$

$$C_m = (S_m - S_{bl}) / m = kS_{bl} / m$$

Where, S is sample signal, S_{bl} is the average of blank signal, s_{bl} is the standard deviation of blank, C is sample concentration, and m is slope of calibration curve or calibration sensitivity, The subscript "m" means minimum.

Detection limits for some oxygenated and chlorinated VOCs are presented in Table 5. The detection limit was computed as three times the signal to noise ratio. Detection limit were computed for two source, #1 and #2. Source #2 was new and showed lower detection limits. Source #1 had been used for several months and showed much higher detection limits. It appears that the response decreases over long periods of operation. The detection limit for most of these levels is rather high considering the fact that at such a high source current the selectivity is low. To get higher selectivity, source current will have to be decreased and this will raise the detection limits. This seems to be one of the major limitations of this detector in trace analysis applications.

5.3 Evaluation of TID

TID is stable enough to maintain the reproducibility of its response to analytes. The TID/FID ratio does not change much with the sample concentration. The response ratio of these two detectors did not change on day to day basis, regardless of the injection amount. However, the lifespan of the thermionic source is limited. As the source is exhausted, the response of TID decreases. Near the end of its life, the response of TID to the same compound may change significantly. The operating lifetime of the source generally decreases with increasing source current.

Table 5 Detection Limit of TID for Some Compounds

Compound	Detection Limit (ng)	
	#1	#2
Oxygenated		
Methanol	1.69	0.09
Ethanol	1.36	0.09
1-Propanol	0.95	0.09
Acetone	1.88	-----
MEK	0.96	-----
MIBK	0.86	0.29
Methyl Acetate	2.61	0.43
Ethyl Acetate	2.11	0.04
Nitrogenated		
Acetonitrile	0.06	0.10
Halogenated		
Epichlorohydrin	0.30	0.04
Methyl Chloride	1.72	-----
1,2-Dichloroethane	0.13	0.04

CHAPTER 6

CONCLUSIONS

The TID responded to oxygenated and chlorinated compounds, both of which are important from an environmental stand point. Oxygenated VOCs were of interest in this study and the TID was found to respond selectively to these compounds in presence of different hydrocarbons. Compared to other selective GC detectors such as ECD and NPD, this TID showed low selectivity and sensitivity for oxygenated compounds. Although for trace air analysis at ppb_v levels higher sensitivity is desirable, this detector can be very useful for higher concentration samples. There is a trade-off between sensitivity and selectivity depending upon source current which needs to be adjusted based on the requirements of the analysis.

APPENDIX A

FIGURES FOR CHAPTER 1

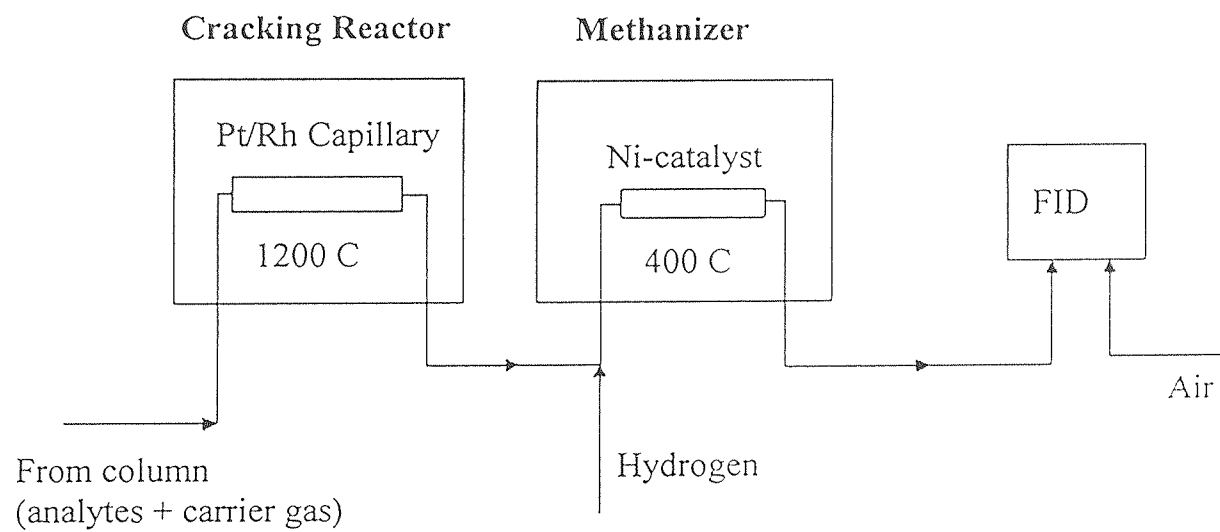


Figure 1 Oxygen-sensitive flame ionization detector

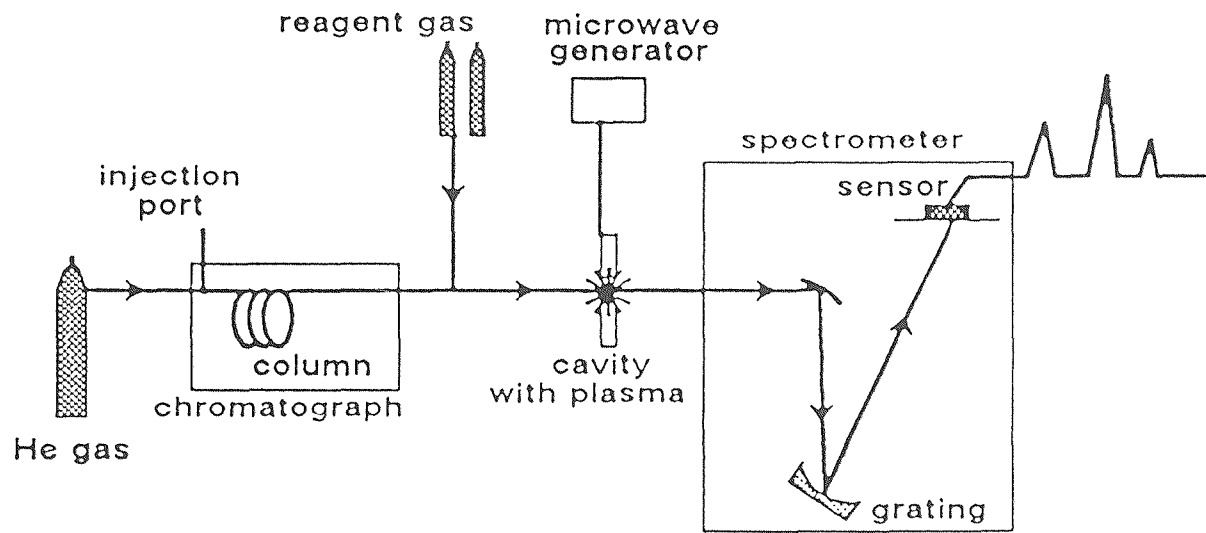


Figure 2 Atomic emission detector

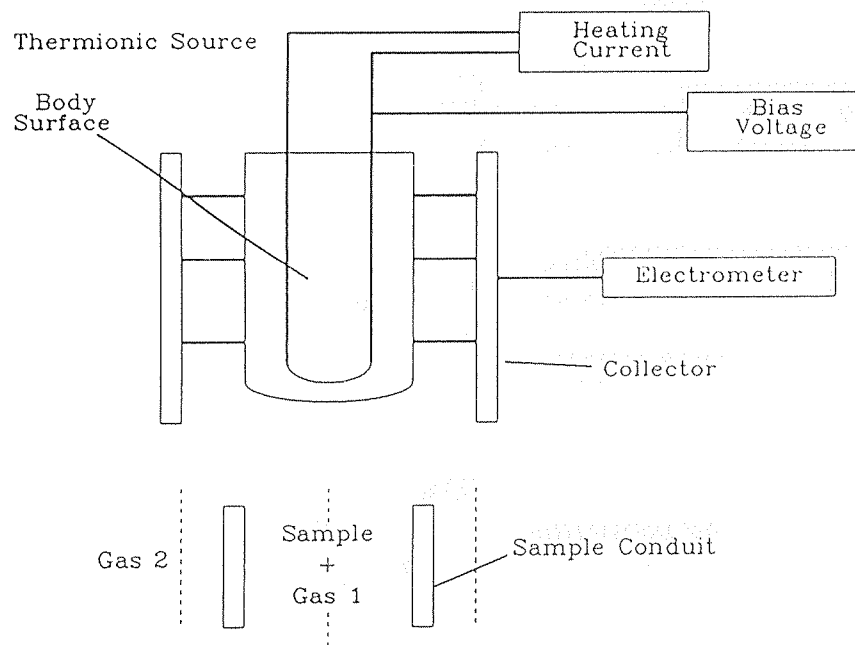


Figure 3 Thermionic ionization detector

APPENDIX B

FIGURES FOR CHAPTER 4

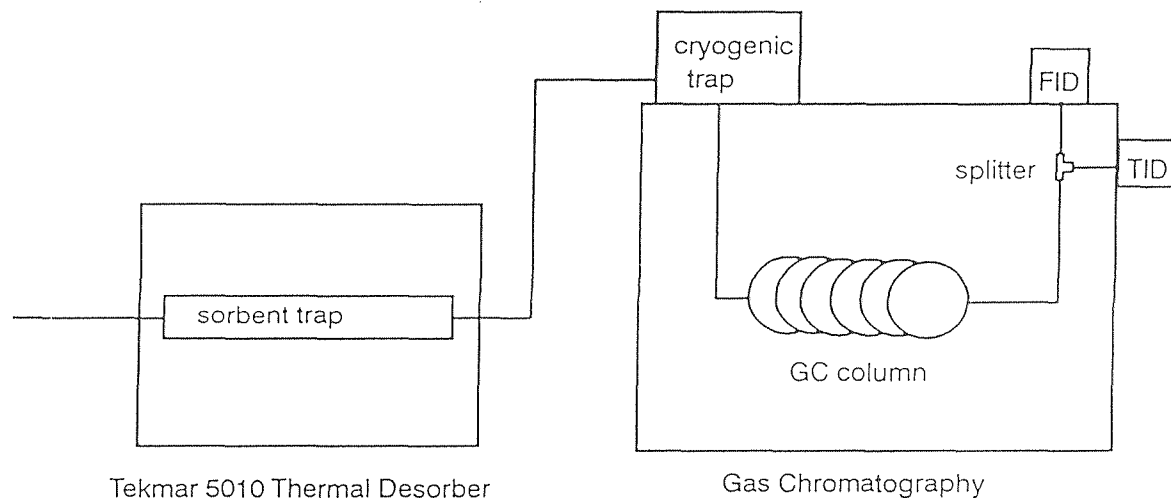


Figure 4 Schematic diagram of the analytical system

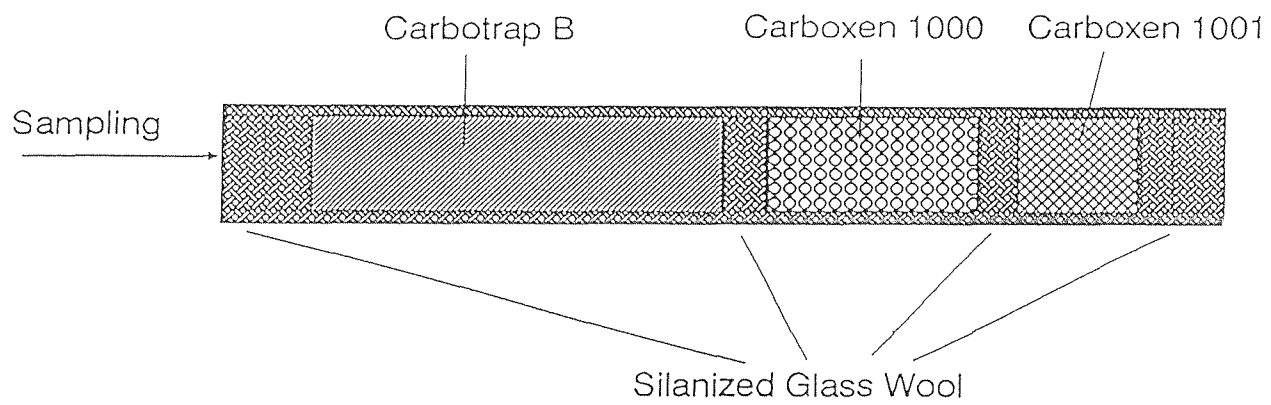


Figure 5 Sorbent trap containing multiple beds of adsorbents

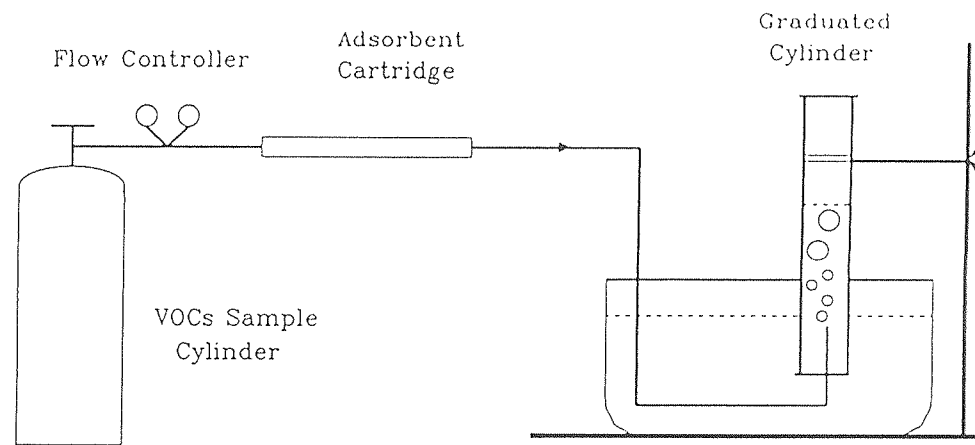


Figure 6 Gas sampling apparatus

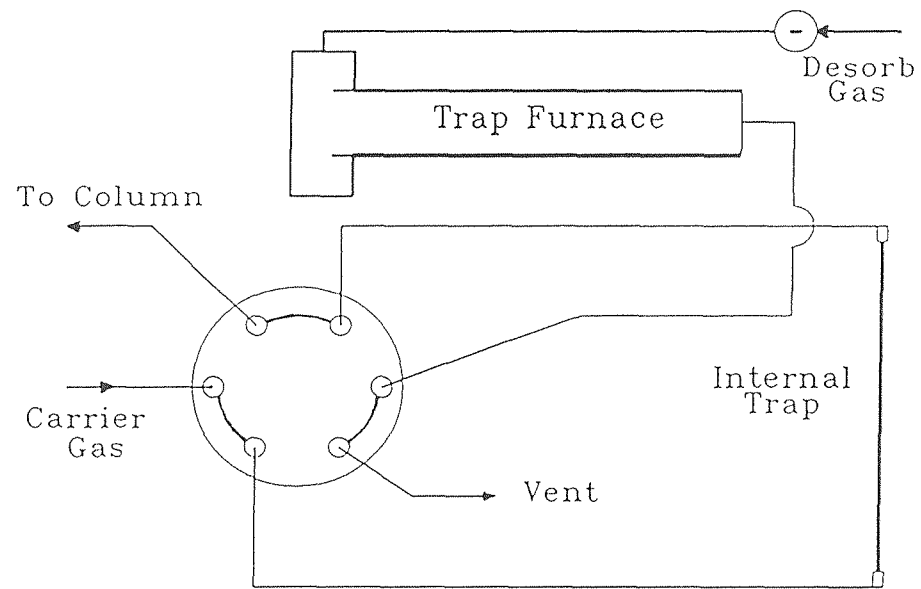


Figure 7 Gas flow system of thermal desorber

APPENDIX C

FIGURES FOR CHAPTER 5

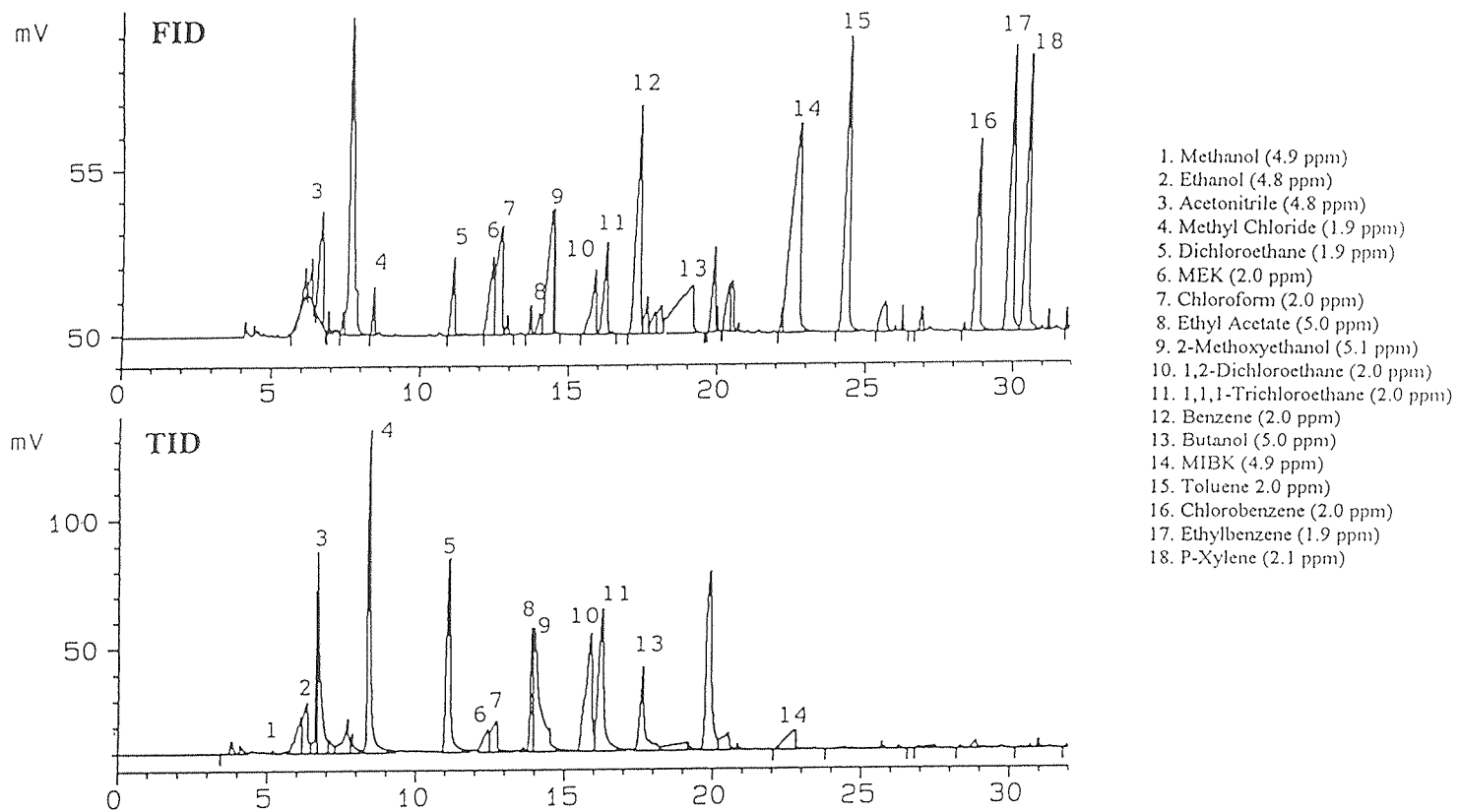


Figure 8 Selective detection of VOCs in standard gas I by TID

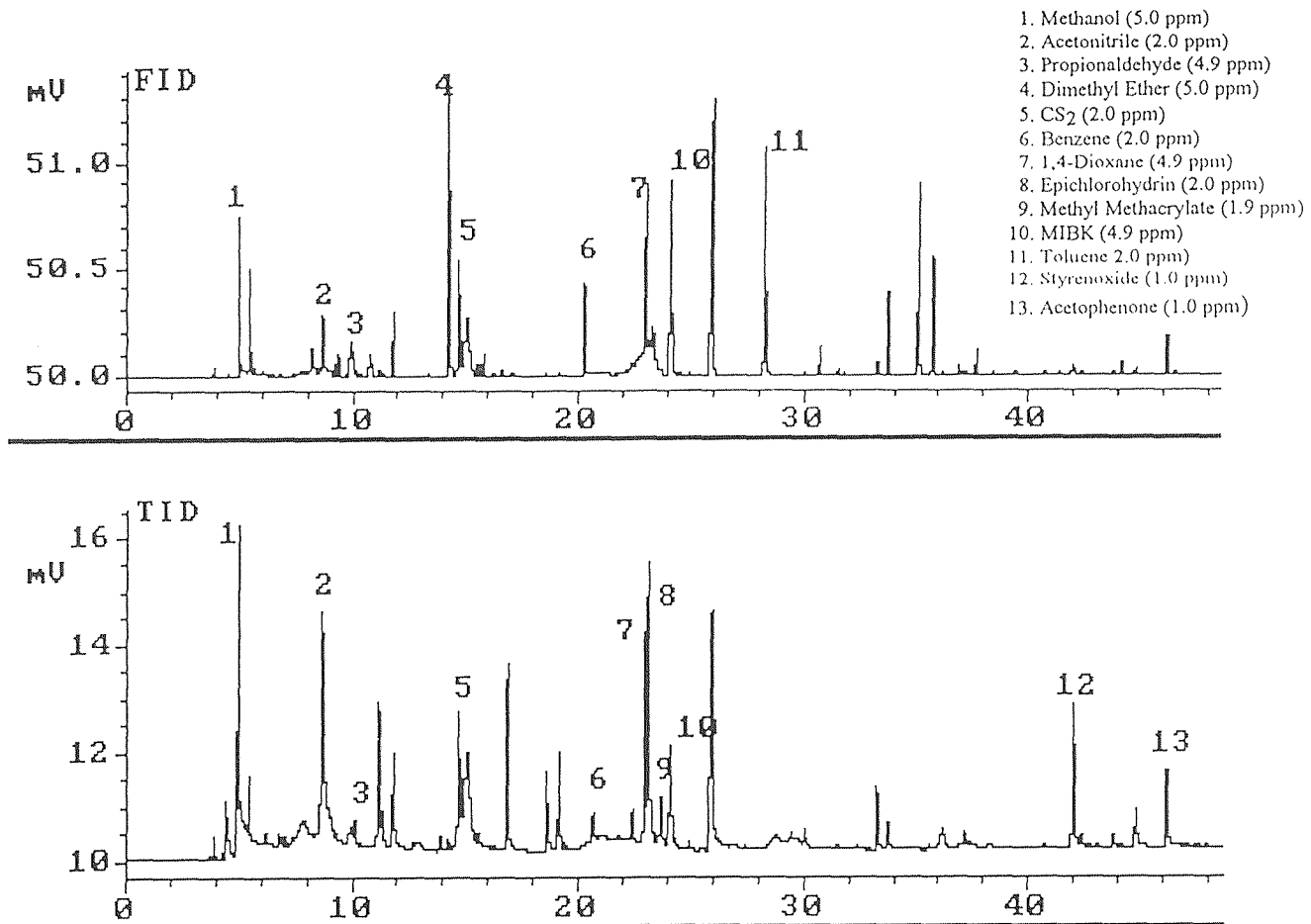


Figure 9 Selective detection of VOCs in standard gas II by TID

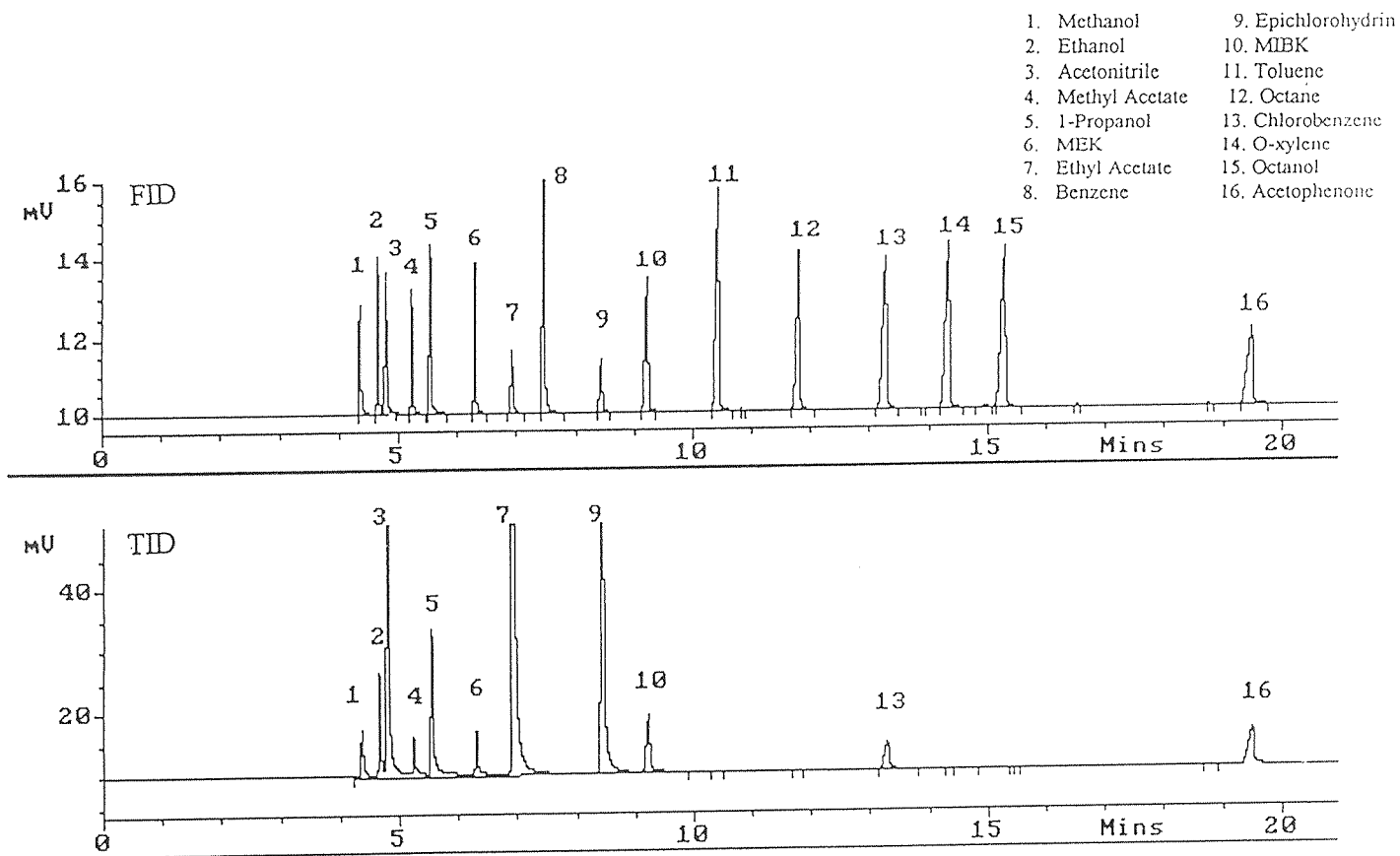


Figure 10 Selective detection of VOCs in liquid mixture by TID

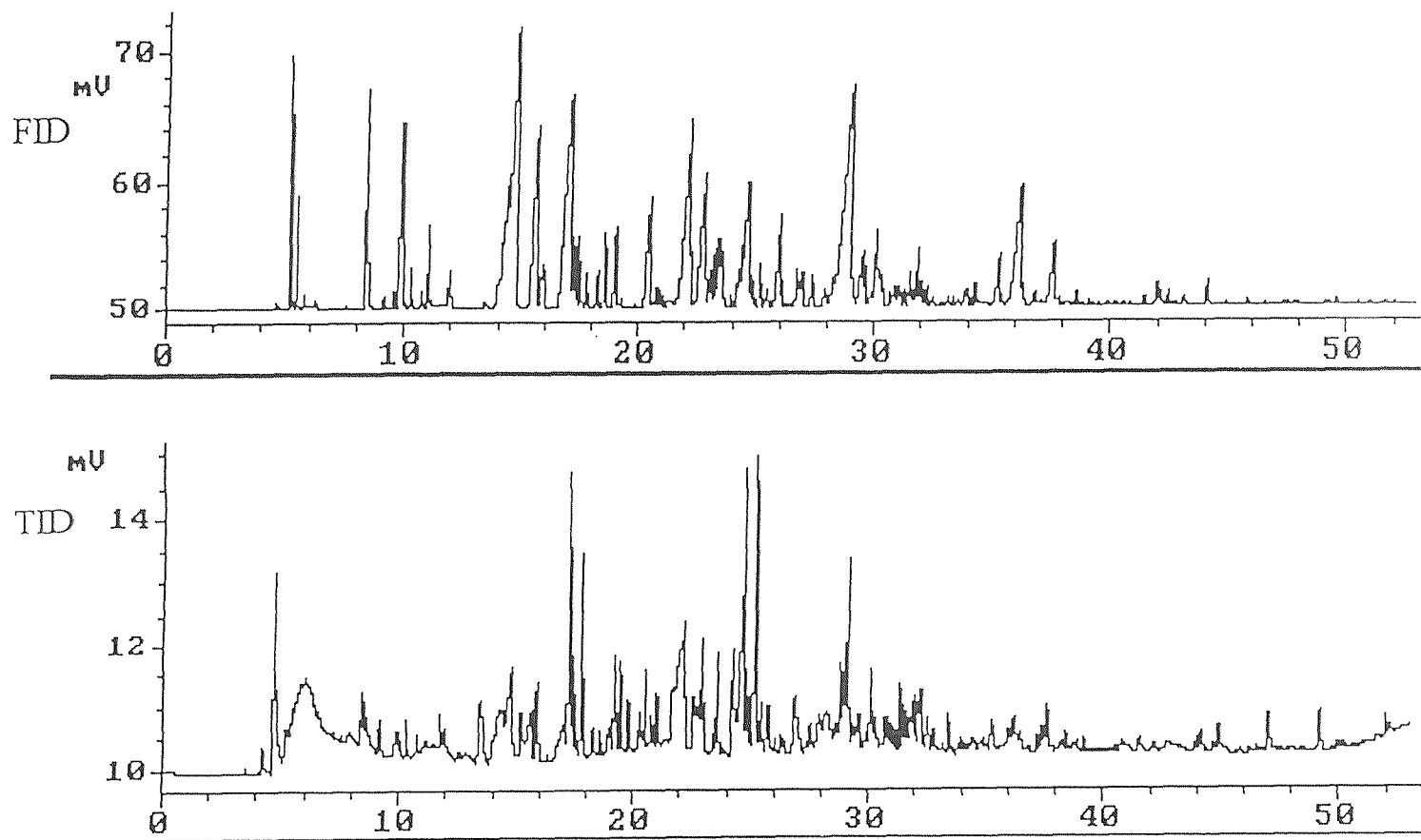


Figure 11 Detection of VOCs in gasoline head space by FID and TID

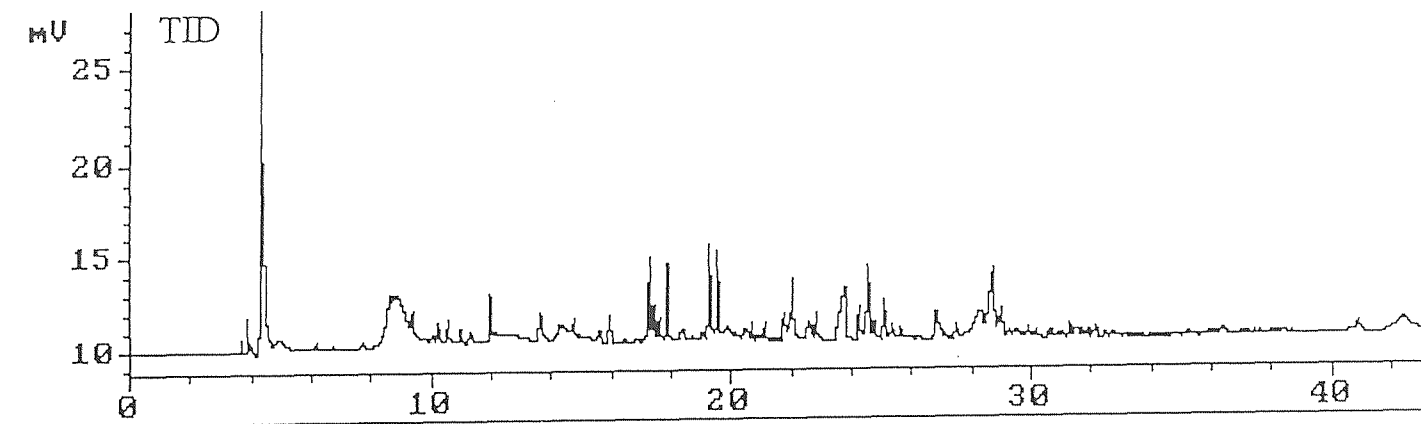
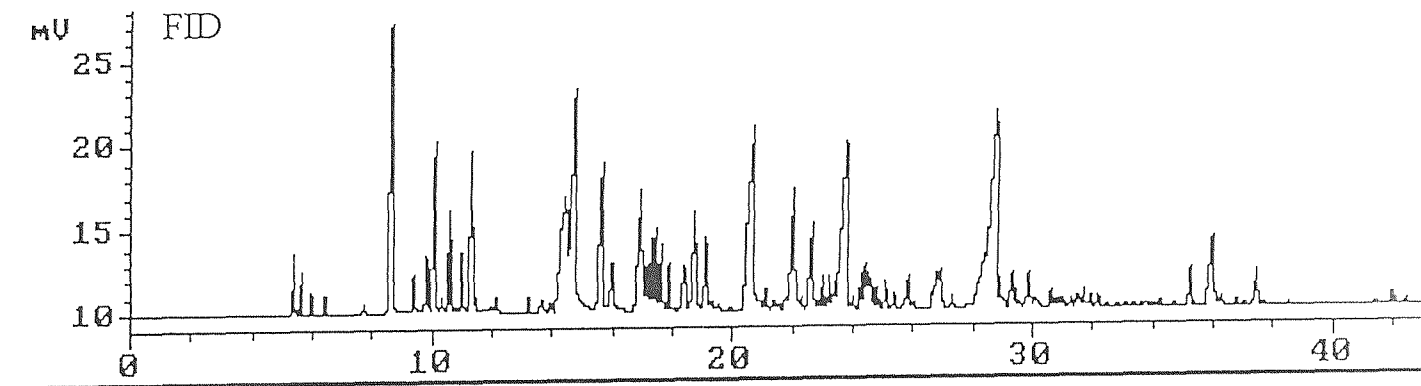


Figure 12 Detection of VOCs in auto exhaust by FID and TID

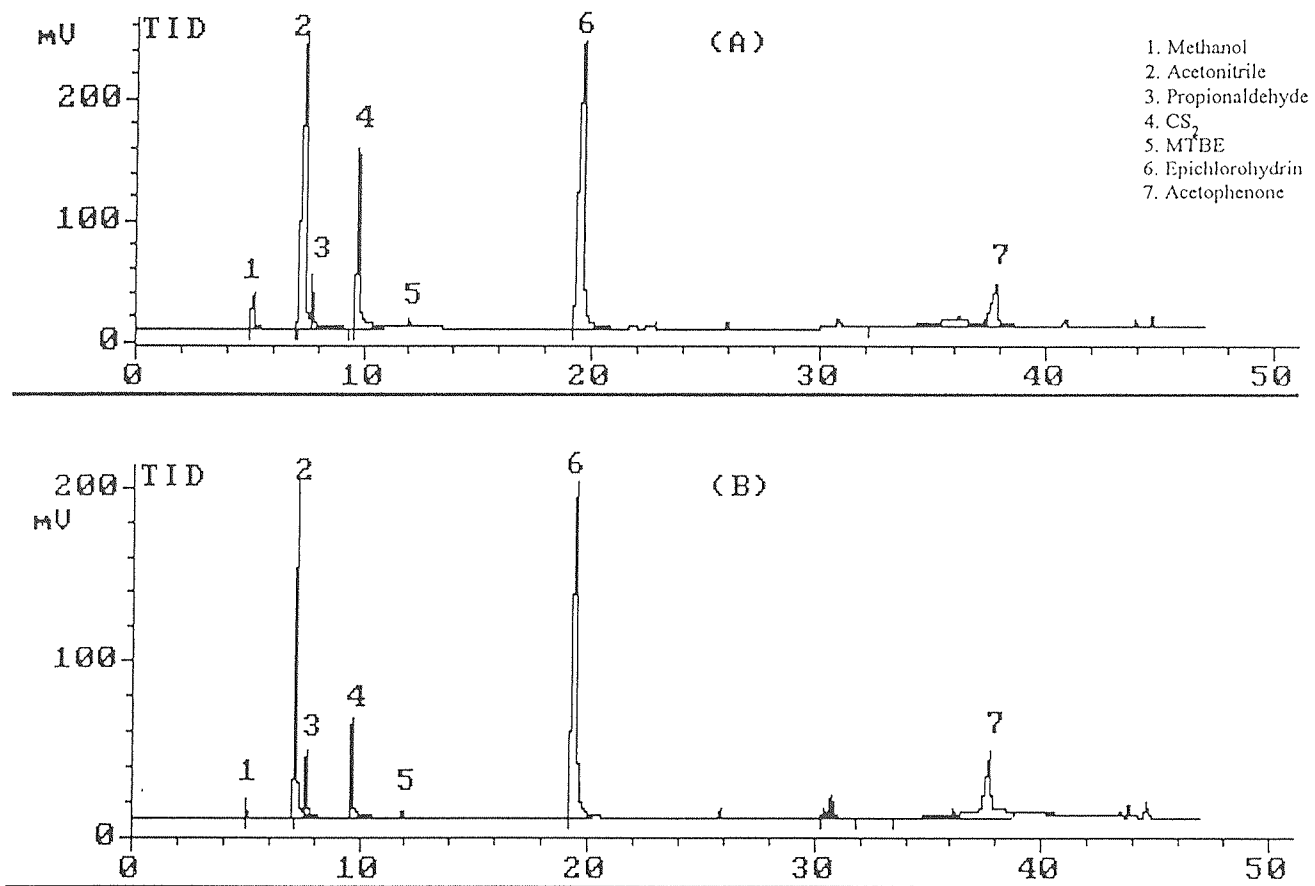


Figure 13a TID response for Water-VOCs Mixture:
 A) With No Water; B) With 50% Water

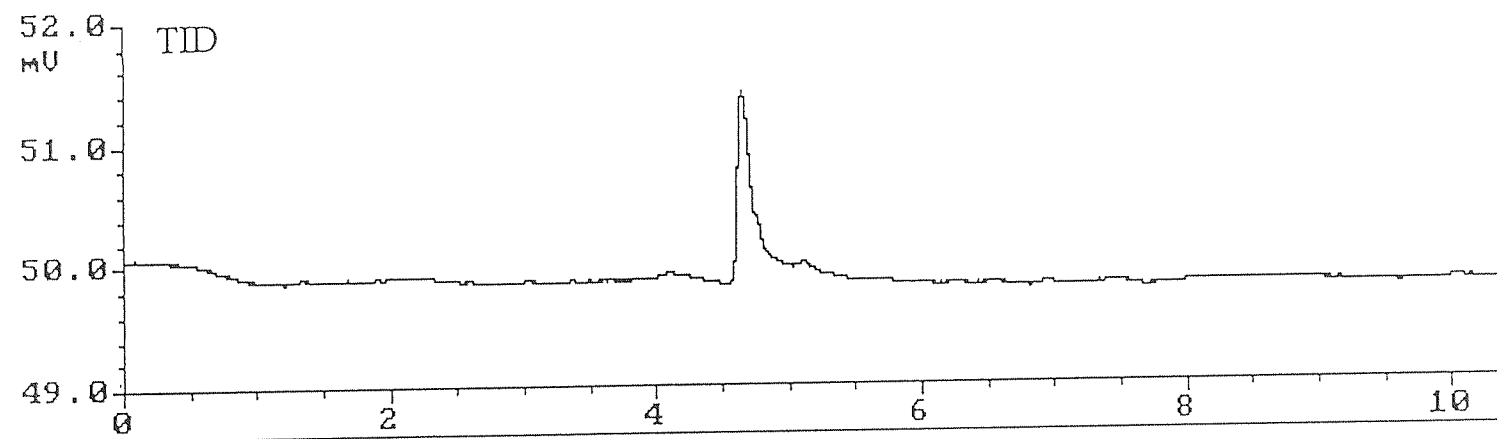
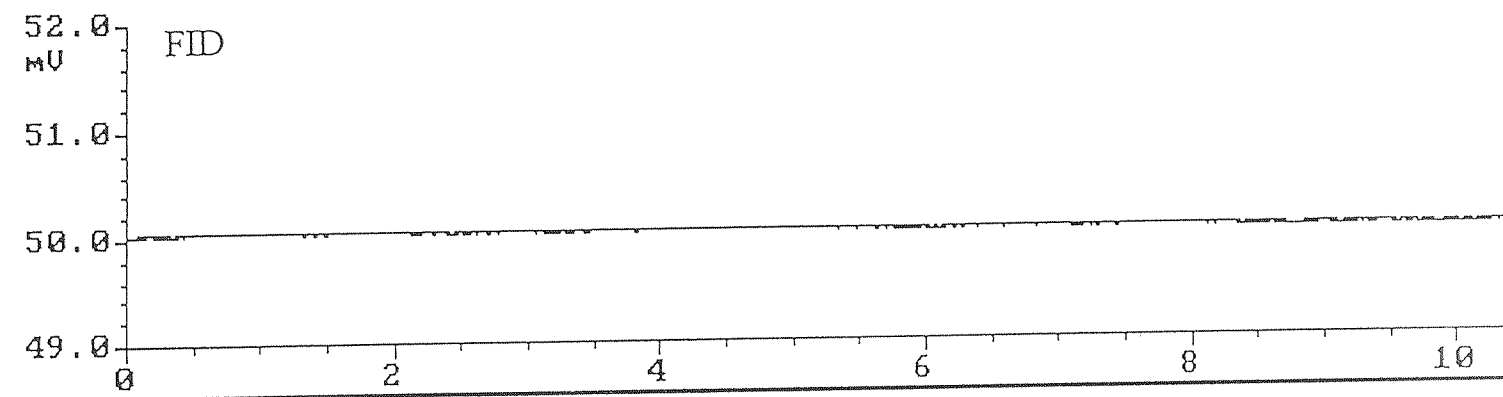


Figure 13b TID response to water (100%)

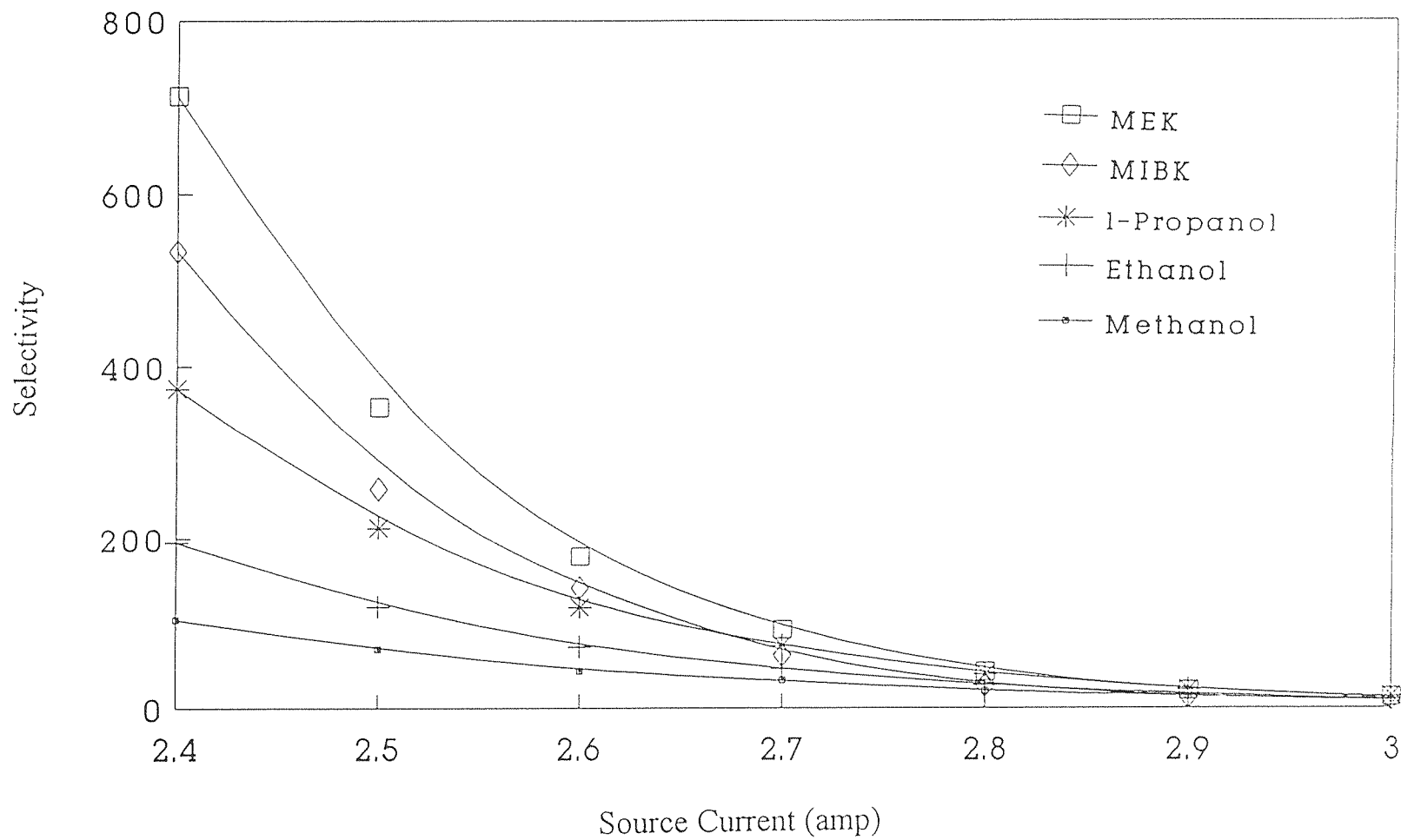


Figure 14a Effect of source current on selectivity (with respect to hexane)

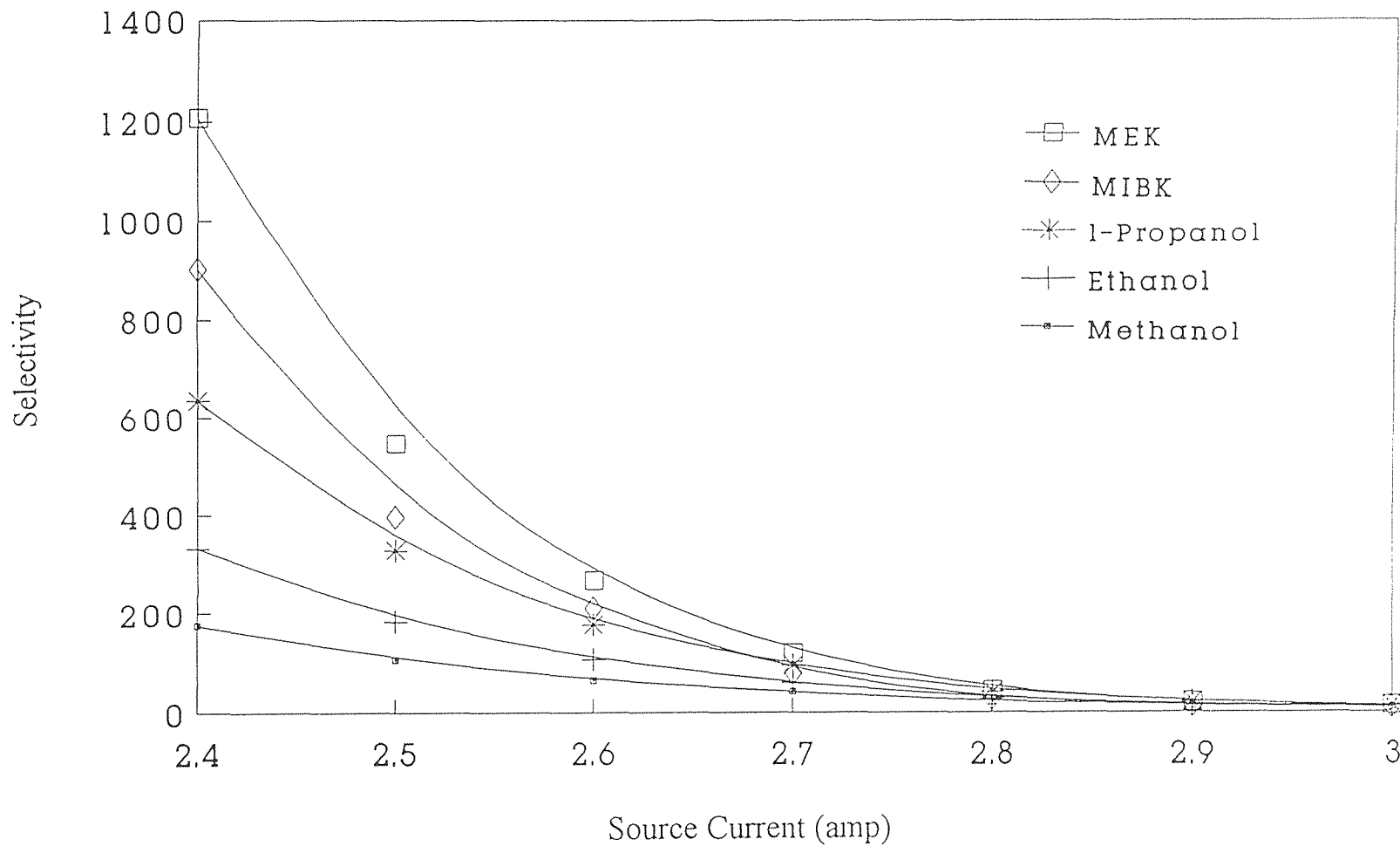


Figure 14b Effect of source current on selectivity (with respect to pentane)

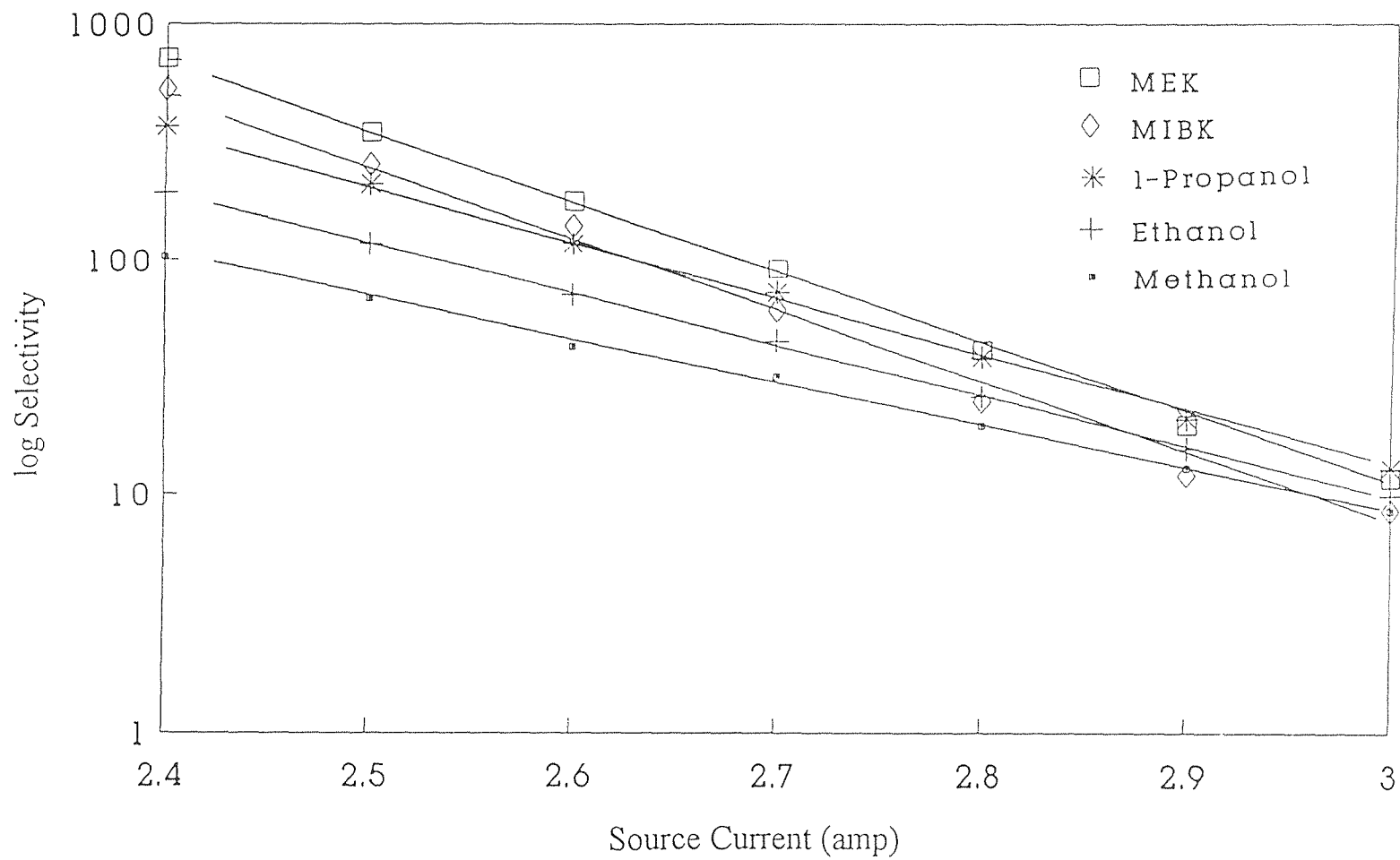


Figure 15a Effect of source current on selectivity (with respect to hexane)

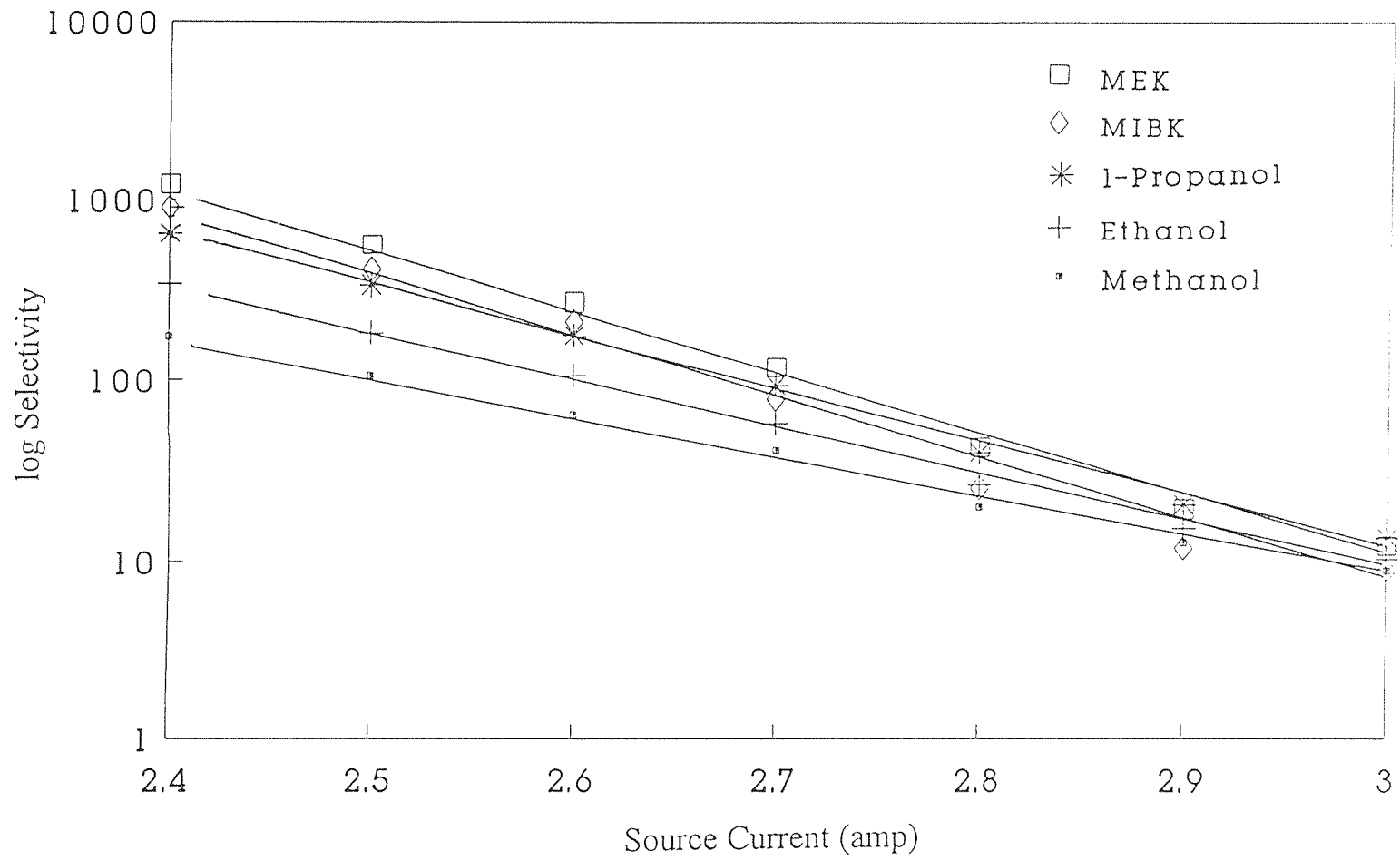


Figure 15b Effect of source current on selectivity (with respect to pentane)

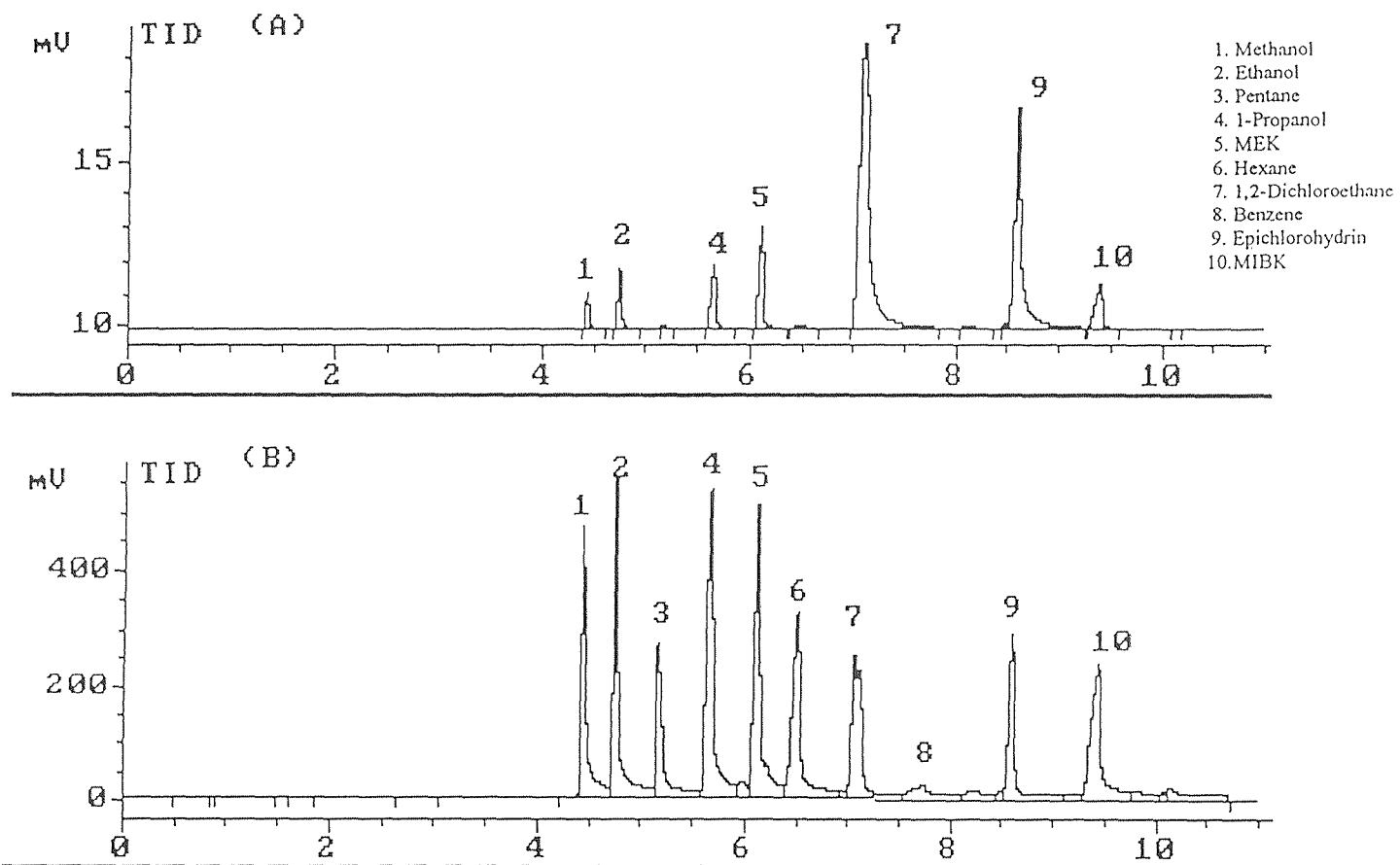


Figure 16 Effect of source current on TID response:

A) Source current of 2.6 amp; B) Source current of 3.0 amp

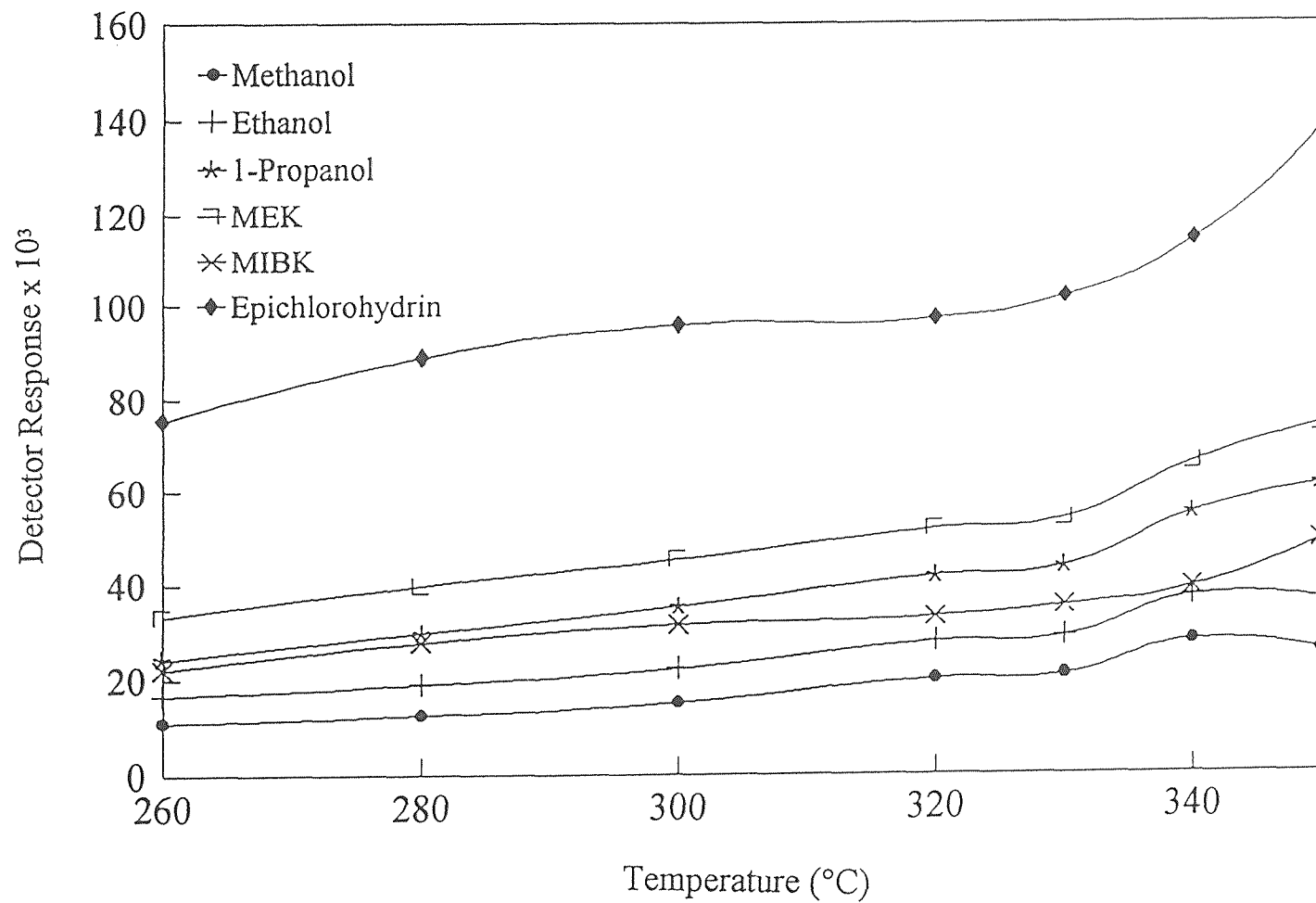


Figure 17 Effect of detector temperature on TID response

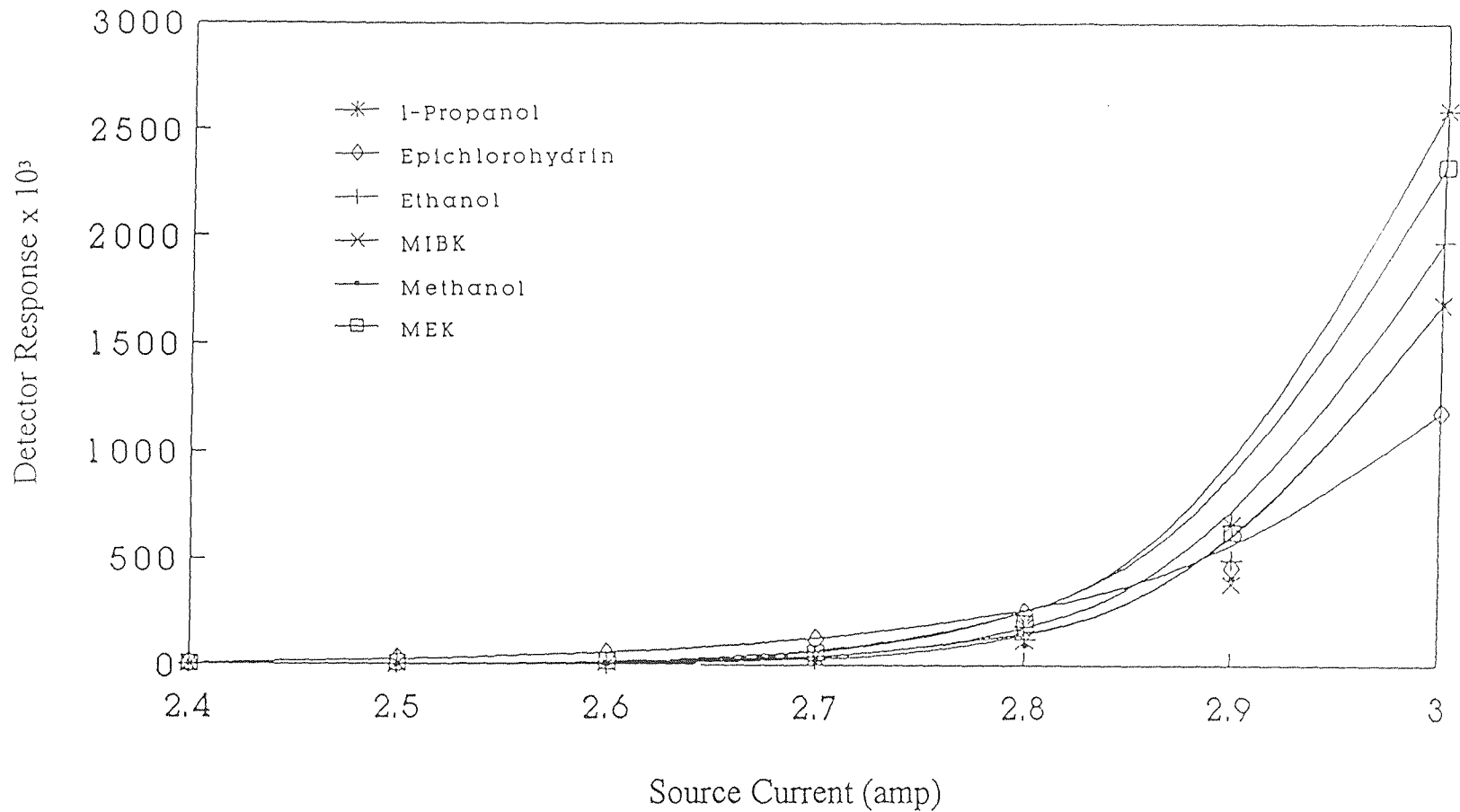


Figure 18 Effect of detector current on TID response

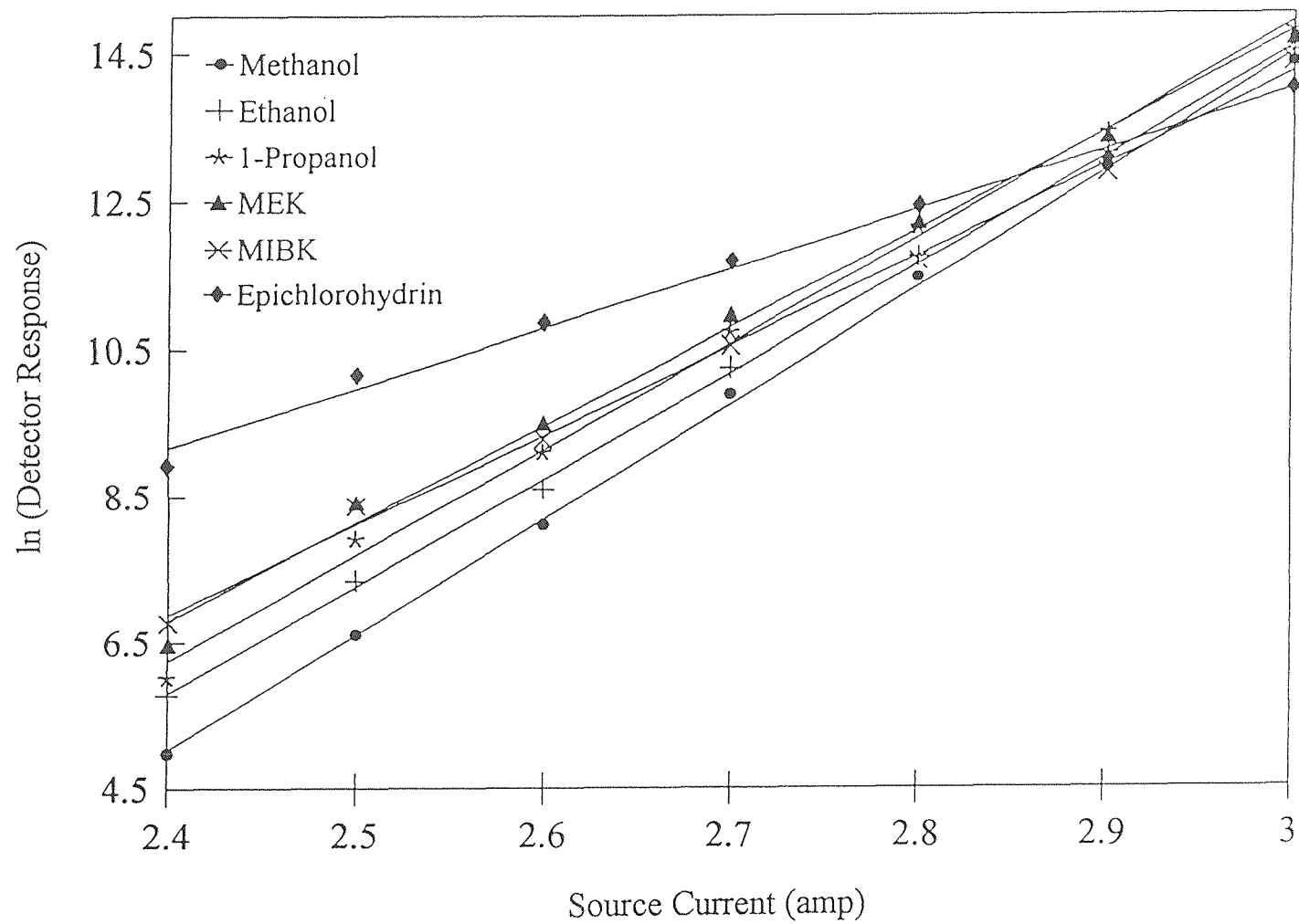


Figure 19 Effect of detector current on TID response

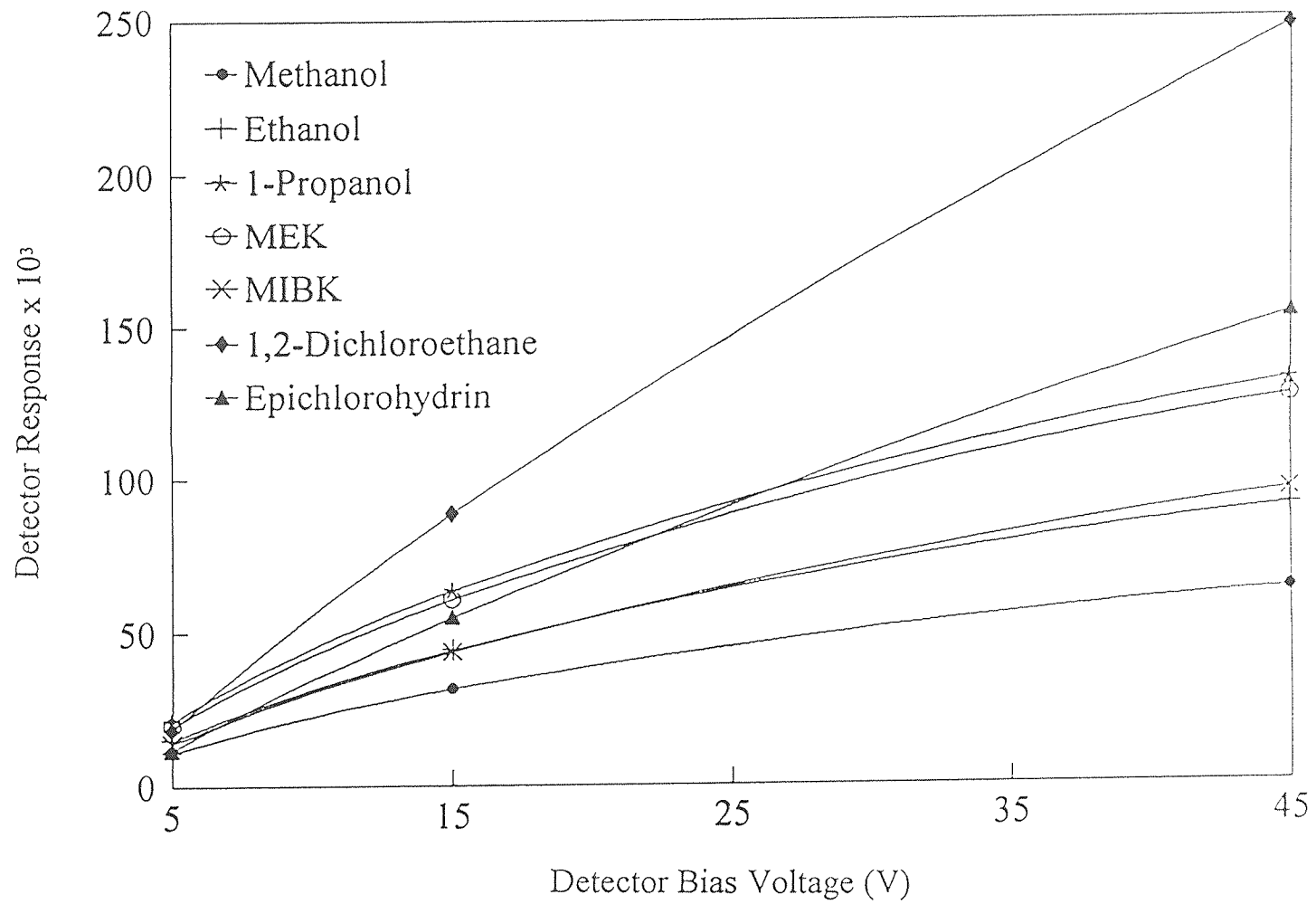


Figure 20 Effect of bias voltage on TID response

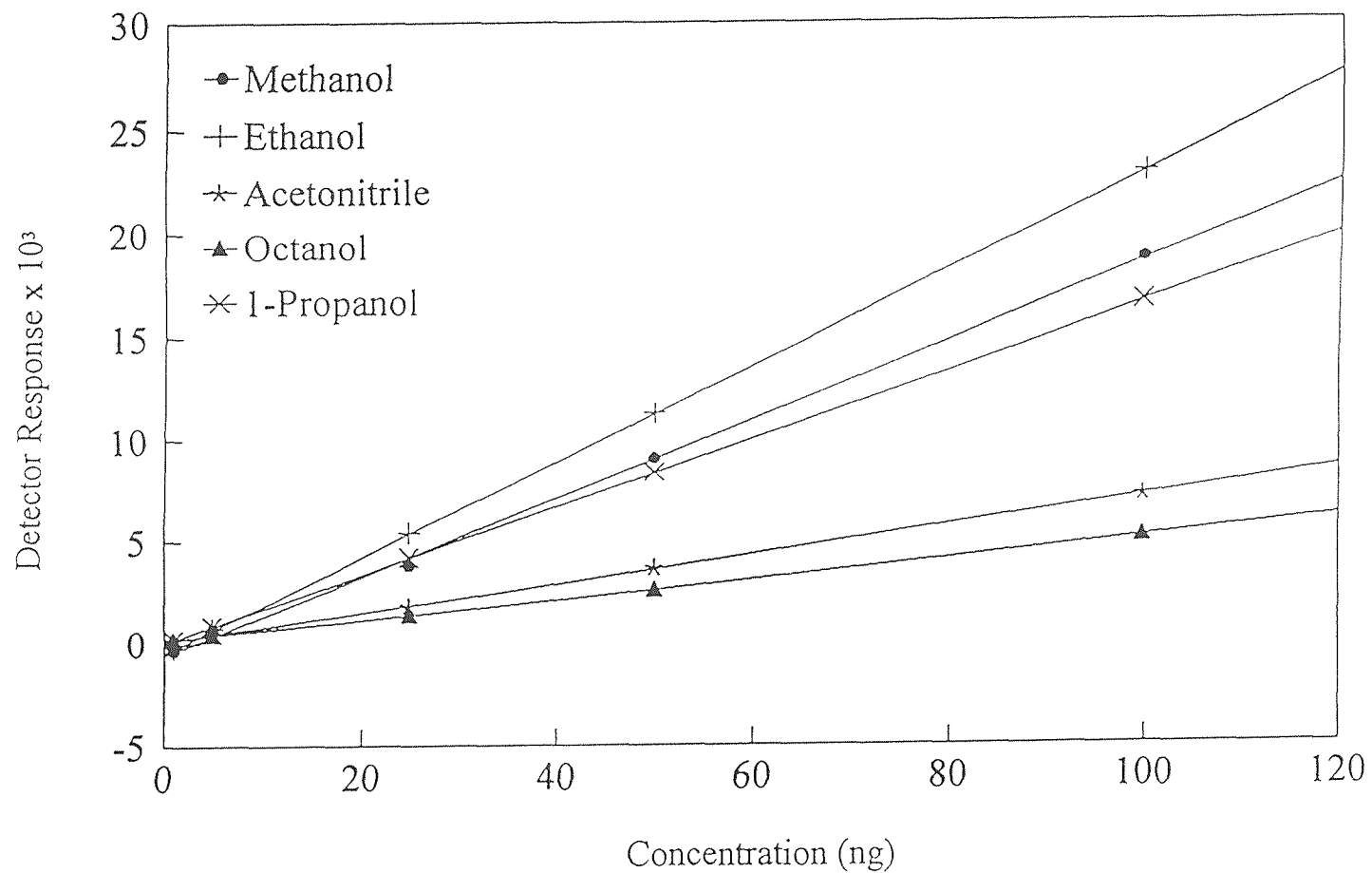


Figure 21 Calibration curve of TID response

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